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A MULTIPLE PHOTODIODE ARRAY DIRECT READING SPECTROMETER FOR EMISSION SPECTROSCOPY

by

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ABSTRACT

The replacement of the photographic spectrograph by the electronic direct reader has greatly improved the quality of elemental analysis by atomic emission spectroscopy. In making the change, two useful characteristics of the spectrograph were lost. These were the relative ease with which new analytical problems could be tackled, and direct information about the background against which the intensity of a spectral line was measured. Both of these losses were due to the replacement of a detector measuring a continuous spectral range by a series of discrete, single wavelength detectors.

The photodiode array is a solid state imaging device, and when it is used as a detector as a replacement for the photomultiplier tube, it allows the measurement of a spectral window rather than just a single line. This restores the versatility and knowledge of the spectral background previously lost.

The design, construction and testing of a direct reading instrument based on short segments of photodiode array are described. Detection limits for the array are shown to be approximately equivalent to those of the photomultiplier tube system.

A technique is developed for controlling, and receiving data from several photodiode arrays with a single microcomputer.

The new instrument demonstrates solutions to some of the background problems of the direct reader. Its versatility as an analytical tool is demonstrated by its rapid adjustment to solve an analytical problem.

Finally, the problems associated with the new system are described and suggestions for their solution proposed.

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CHAPTER I

INTRODUCTION

1. The Direct Reader

The direct reader is a spectrometer for determining the concentrations of several elements by simultaneous, direct measurement of the intensities of their atomic emission spectra.

The spectral intensities are measured electronically and converted to numerical values which are related to the elemental concentrations; all without the delay of further processing. This is in contrast to the spectrograph which requires the time-consuming processing of photographic film and subsequent skilled interpretation.

The electronic recording of atomic emission intensities was forcast by Harrison in 1940 [1]. Early experiments were made by Duffendack in 1942 [2] who found that a Geiger counter could be made to respond to that part of the ultra violet region with wavelengths below 260 nm. By 1945 Saunderson [3] was investigating arc spectra using eleven photomultiplier tubes.

The photomultiplier tube based direct reader, as illustrated by Figure 1, has become the standard instrument for the routine measurement of atomic spectral intensities. To do this, it had to show considerable advantages over the already established photography based spectrograph. These were:-

i. The analytical results were available immediately.
ii. The results were obtained by a less skilled operator.
iii. A higher rate of sample throughput.
iv. Superior accuracy.
v. Superior precision.
vi. Greatly increased linear dynamic range.

The immediate availability of analytical results is very important to metal processors who require such information before making a casting [4]. The lower level of skill needed in the operator combined with the higher throughput of samples reduces the cost of analysis [4].

The superior accuracy, precision and linear dynamic range of the direct reader changed atomic emission spectroscopy from a qualitative, or at best a semi-quantitative, analytical method to a quantitative one. The accuracy improved from about 10% for the spectrograph, with the use of internal standards and a skilled operator, [5] to 1% [6]. Relative standard deviations improved from

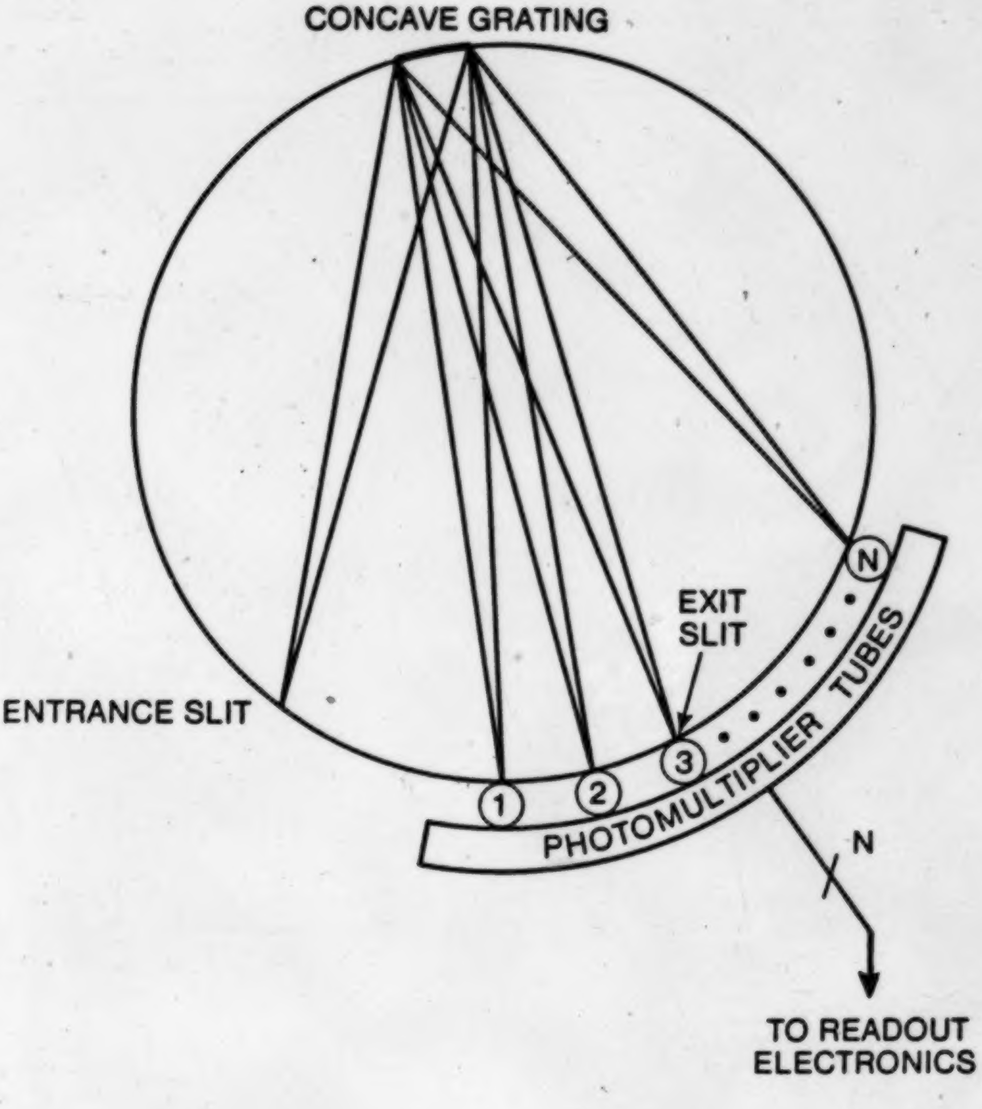
CONCAVE GRATING
ENTRANCE SLIT
EXIT
SLIT
1
2
3
N
PHOTOMULTIPLIER TUBES
N
TO READOUT
ELECTRONICS

Figure 1. The photomultiplier tube based direct reader.

a few percent [7] (about 10%) to 1% or less. The linear dynamic range, with respect to intensity measurement, of the spectrograph is limited to one order of magnitude as the intensity of a spectral line is measured photographically. In contrast, the photomultiplier tube has a linear dynamic range of seven orders of magnitude so that the linearity of the direct reader is generally limited by that of the spectral emission source.

The direct reader has three major disadvantages when compared to the spectrograph. These are due to the replacement of a detector covering a continuous spectral range by a series of discrete detectors. A photographic plate capable of recording 10,000 resolution elements is replaced by a series of exit slits backed by photomultiplier tubes capable of recording only 30 to 60 resolution elements (one per tube). These disadvantages are:-

i. Limited and restricted wavelength coverage.
ii. Lack of versatility.
iii. Limited background correction.

2. The Versatility Problem

With the spectrograph, detection of an additional element involved the selection and subsequent interpretation of a suitable spectral line within the wavelength range of the instrument. With the direct reader it is much more difficult.

The placing of the exit slits in the focal plane has to be very accurate as they are only 20-50 μm wide and have to be centred on the analyte line. Addition of a detector for a new element without adverse effect on those already in place requires technical input from the instrument's manufacturer. The close packing of the exit slits is limited by the need for the slits to have boundaries and particularly by the absolute width of the photomultiplier tubes. Although a pair of closely spaced spectral lines can be separated by accurately positioned plane or prism shaped mirrors, close packing of the detectors is a limiting factor in the selection of spectral lines. The spectrograph is a general purpose instrument. The direct reader is almost always custom built. The user has to specify the elements to be analyzed for, or that are likely to be present in all matrices to be investigated, when ordering the instrument. The instrument supplier then must design the direct reader focal plane array to suit, taking into account his own limitations.

In order to return partially to the concept of versatility, manufacturers have taken to fitting the focal plane with slits or slit holders for most of the elements usually sought after, and supplying detection systems and detection system optics, such as mirrors and wavelength selection filters, for those elements specified by the customer. In order to give the user some versatility, at least one manufacturer has combined a monochromator with a direct reader. Part of the light generated by the spectral source enters a scanning monochromator that can be preset to any particular wavelength by an operator [8]. The single photomultiplier tube of the monochromator is coupled to the direct reader electronics as an effective extra channel.

3. The Background Correction Problem

Another major disadvantage of direct readers is their lack of data on background radiation against which the strength of the emission line can be measured.

The background radiation has two origins:-

i. Stray light.
ii. Spectral interferences.

3.1 Stray Light

Stray light has been broadly defined as "The unwanted radiation that reaches the detector in unintended ways" [9]. It is caused by defects in the instrument which may be in the quality of the grating or in the rest of the instrument.

When a master grating is made on a ruling machine, the diamond cutting tip is advanced by a lead screw. Imperfections in the lead screw give periodic errors in the spacing of the grooves on the grating and these are reproduced in the replicate gratings. This causes the formation of secondary images, known as Rowland ghosts, that are spaced symmetrically about the parent line [10]. If the ruling is subjected to an external periodic vibration, the grating forms other secondary images called Lyman ghosts at a large distance away from the parent line [10].

Light is scattered from the surface of the grating. Near scatter (below 5 nm from the parent line) is the effect of random disturbances of the ruling machine. Far scatter (more than 5 nm from the parent line [9]) is due to microscopic imperfections in the grooves or the grating blank. The diamond tipped cutter of the ruling machine may deform the edges of the grooves as it makes them, by pushing up the material displaced by the cutter, and this roughness adds to the far scatter [11]. Some gratings are now being made without the use of ruling machines by photographically recording the interference pattern obtained from two beams of monochromatic (laser) light [10]. Such holographically recorded gratings do not exhibit ghosts and consequently have much lower stray light levels than ruled gratings [9,10].

Apart from the grating, there are other causes of stray light inside the direct reader light-proof box. Reflection of both primary (undiffracted) and diffracted light off the interior surfaces of the system can cause far scatter and general background stray light. Because they are directly in the path of the spectral line, the edges of exit slits and the photomultiplier tubes themselves can cause scatter [9].

Instrumental line broadening is caused by the finite width of the slits, optical misalignments and optical aberrations. This can cause overlap of closely spaced spectral lines [9].

3.2 Spectral Interferences

Spectral interferences are generated when light generated by a spectral source is processed by an ideal grating. There are two classes of spectral interference:-

i. Produced by the grating, where the interfering radiation will have a different wavelength to that of the analyte line.

ii. Produced in the spectral source so that the interfering radiation has the same wavelength as the analyte line.

The grating produces multiple orders of spectral lines and these are routinely used by direct reader designers to help overcome detector spacing problems.

Wavelength selective transmission filters are used to differentiate between the various principal orders. The grating also forms secondary interference maxima of much lower intensity than the principal ones. These may become significant in the future as instrumental defects are eliminated but at present they are of little significance [12].

Spectral interferences produced in the spectral source are a much more serious problem as they have the same wavelength as the analyte line but are generated by other species. The other species can be part of the carrier or excitation system of the source, or they may be concomitant species supplied by the analytical sample matrix. Carrier generated interferences are source dependent and may be of a molecular nature. For example, cyanogen bands may be generated by a DC arc source, C_2 and CH bands by a flame source and nitric oxide bands by an inductively coupled argon plasma. Additionally, all systems where an aqueous solution of the sample is nebulized generate hydroxyl bands.

The atomic emission lines for the elements in the carrier also occur in the spectrum, often with variable intensities. Examples are carbon lines in DC arc and argon lines with the ICP.

Concomitant generated interferences are of several kinds. These are direct line overlap, wing overlap, and, with the inductively coupled argon plasma source, recombination continua [13]. Direct line overlap occurs where a concomitant element has a spectral line too close to that of the analyte for the instrument to resolve. Wing overlap occurs when the concomitant and analyte lines can be resolved but the spectral profiles of the lines overlap sufficiently for the intensity of the analyte line to include some portion of that of the concomitant. Recombination continua are generated by the radiative recombination of certain metal ions with the high concentration of electrons in the argon plasma. Strong continua are formed by magnesium, calcium and aluminum that alter spectral base lines below 250, 302 and 220 nm respectively [12].

The major problem of concomitant generated interference is that the concomitant concentrations are, like those of the analyte elements, part of the unknown in the analyte sample. When concomitant species are in much higher concentration than the analyte, they can cause special problems. A spectral line of an element, present at a trace level, can suffer overlap from a minor spectral line of the concomitant that only becomes significant because of the great differences in the concentrations.

Large concentrations of strongly emitting concomitants are also the major sources of instrumental stray light.

In summary, the light intensity detected for the analyte spectral line may not be proportional to the analyte concentration because it is measured against an unknown and variable radiative background.

4. Current Background Correction Methods

Current methods of correcting for background radiation can be described as either off-peak or on-peak methods.

4.1 Off-peak Methods

Off-peak methods are made by sampling the background on one or both sides of an analyte line, just outside the instrument band pass.

For example, a direct reader with an exit slit 50 µm wide and a reciprocal dispersion of 0.53 nm per mm would have a band pass of 0.0265 nm and the background would be sampled at line +0.034 nm [14]. The correction is made by altering the angle at which the incident light meets the grating, so that all of the detector channels are effectively shifted off all of the analyte lines by the same distance, and then taking a second set of intensity measurements.

One of two mechanisms is generally employed. In one, a quartz refractor plate located just behind the entrance slit of the direct reader is rotated to shift the effective position of the slit sideways with reference to the grating. This requires a high degree of precision in the control of the angle change and may change the level of light transmitted due to the change in reflectivity at the plate surface as it is turned [15]. The other method involves physically moving the entrance slit sideways. This again has to be carried out with precision and gives rise to the problem that the same portion of the plasma source is no longer being sampled. It has been shown by Blades and Horlick [16] that the intensity profile of the spectral lines emitted from the plasma is laterally position dependant so the background measurements may be inaccurate.

Off-peak correction requires an extra measurement at each detector. As these must be at different times, it requires that the source be a stable one such as an inductively coupled plasma using nebulized sample solutions. It corrects for continuum radiation and general stray light. The species causing the background need not be known. It cannot correct for spectral line overlap and is very vulnerable to the presence of an unanticipated line interference on any of the analyte channels.

4.2 On-peak Corrections

On-peak corrections are more complicated. Prior to the analysis, the response of all detector channels is obtained to a range of concentrations of the concomitant elements. All likely concomitants must be considered. Working curves are prepared for all channels in terms of apparent concentration of analyte against actual concomitant concentration. During the actual testing of the analytical sample, measurements of the concomitants are obtained on separate channels and the corrections calculated from the working curves and subtracted from the analyte values. However, in order to do this, the interfering concomitant must have its own channel on the direct reader. That is to say that it had to be considered at the time the instrument was ordered. This is the reason for specifying all the analytical matrices to be tested when the focal plane array is being designed.

Provided that all of the concomitants are determined, on-peak correction is more accurate than the off-peak method. It is the only way to correct for direct spectral overlap. It requires that the position of all the exit slits be stabilized with respect to the diffraction grating and the entrance slit. This requires that the temperature of the instrument be thermostatically controlled.

The background correction problem was forseen while the instrument was in the early stages of development. Hasler and Dietert [4] forecast the problem in 1944 and Saunderson [3] attempted background measurements in 1945 by using a wire to divide the exit slit into two parts, and diverting the background for measurement.

The off-peak correction method requires two or three sets of measurements for each analysis. An alternative is to scan across each analyte line to get a profile of the line and its background in the same manner as the densitometer readout of a spectrograph photographic plate. Brehm and Fassel [17] used such a scanning technique in 1953 because of problems in locating spectral lines especially when the temperature of the instrument changed. A similar approach has led to the development of a possible rival to the direct reader, the slew-scanning monochromator. Here a single exit slit and photomultiplier tube is used and spectral lines are detected sequentially rather than simultaneously. The grating of a monochromator is quickly turned so that the detector receives each line in turn [18]. The rotation of the grating is fast (slew) from one line to the next and then slow as the profile of the line is scanned. It then slews to the next line and so on. The system depends on accurate and fast control of the grating rotation during both slew and scan processes. Because it acts sequentially, it requires a constant analyte signal such as that given by the inductively coupled argon plasma (ICP) using analyte solutions. It cannot handle transient signals.

A major research field in ICP spectrometry is the removal of the sample digestion and dilution step from the analytical procedure by direct sampling of solid analytes. Instead of the steady signal level obtained from a constant analyte solution flow, these methods give a quick intense burst of signal. All analyte spectral intensities must be measured simultaneously and this requires the direct reader used without the option of off-peak correction methods and certainly not the slew-scan system.

5. An Alternative Approach

In order to regain the versatility and knowledge of background levels possessed by the spectrograph the photographic plate must be replaced by a spatially continuous detector, such as an electronic imaging device, not by a series of discrete single measurement detectors.

Electronic image detectors are available configured in either one or two dimensions. The use of a single grating as a spectral dispersion device suggests the use of a one dimensional imaging device such as the linear photodiode array. Two dimensional devices such as the Vidicon are more suitable for the echelle spectrometer, where a coarsely ruled, blazed grating generates high orders of spectra that are then order sorted by a crossed prism to a two dimensional image pattern. Such a system has been built by Wood [19].

Vidicons are read out using an electron beam directed by scanning electric field coils and are subject to lag and bloom. Lag involves the carryover of signal from one readout scan to the next due to incomplete recharging of the sensor during readout [20,21]. Bloom involves the transfer of a very intense signal over adjacent channels due to the overspill of photon generated charge [22].

On the other hand, linear photodiode arrays utilize solid state switching readout. Because they are fully recharged in less than 1 μs, they do not exhibit lag [23]. Blooming is also less of a problem. It is suggested by Talmi and Simpson [23] that charge spillover with diode arrays is a gradual process, proceeding one diode at a time.

The self scanning linear photodiode arrays have been used for spectrochemical measurements for several years [24]. Some of the early applications were in astronomy where they were applied to low light level spectrophotometry [25]. All of these applications have involved one (or at the most two) [26] photodiode arrays located in permanent fixtures. Diode arrays are relatively small, flat devices. The largest array of the "S" series designed for spectroscopy has 1024 diodes covering a sensor length of 25.6 mm. Consequently a single array cannot cover much of the focal plane of a direct reader which may be 1 m in length. Even if much longer arrays were available, they would have to be curved to conform to the shape of the focal plane of the direct reader. Several small, moveable arrays must be used instead.

The concept of such an instrument, illustrated by Figure 2, is given below.

A normal direct reader optical system is used in which light from an external spectral source passes through a single entrance slit and illuminates a single concave, reflecting, diffraction grating. This grating both wavelength disperses and refocusses the light into a series of wavelength separated images of the entrance slit that are focussed on a curved focal plane. In a traditional direct reader, these images would be individually selected by a series of exit slits and the light from each transferred by simple secondary optics to the photomultiplier tube detector. In the conceived

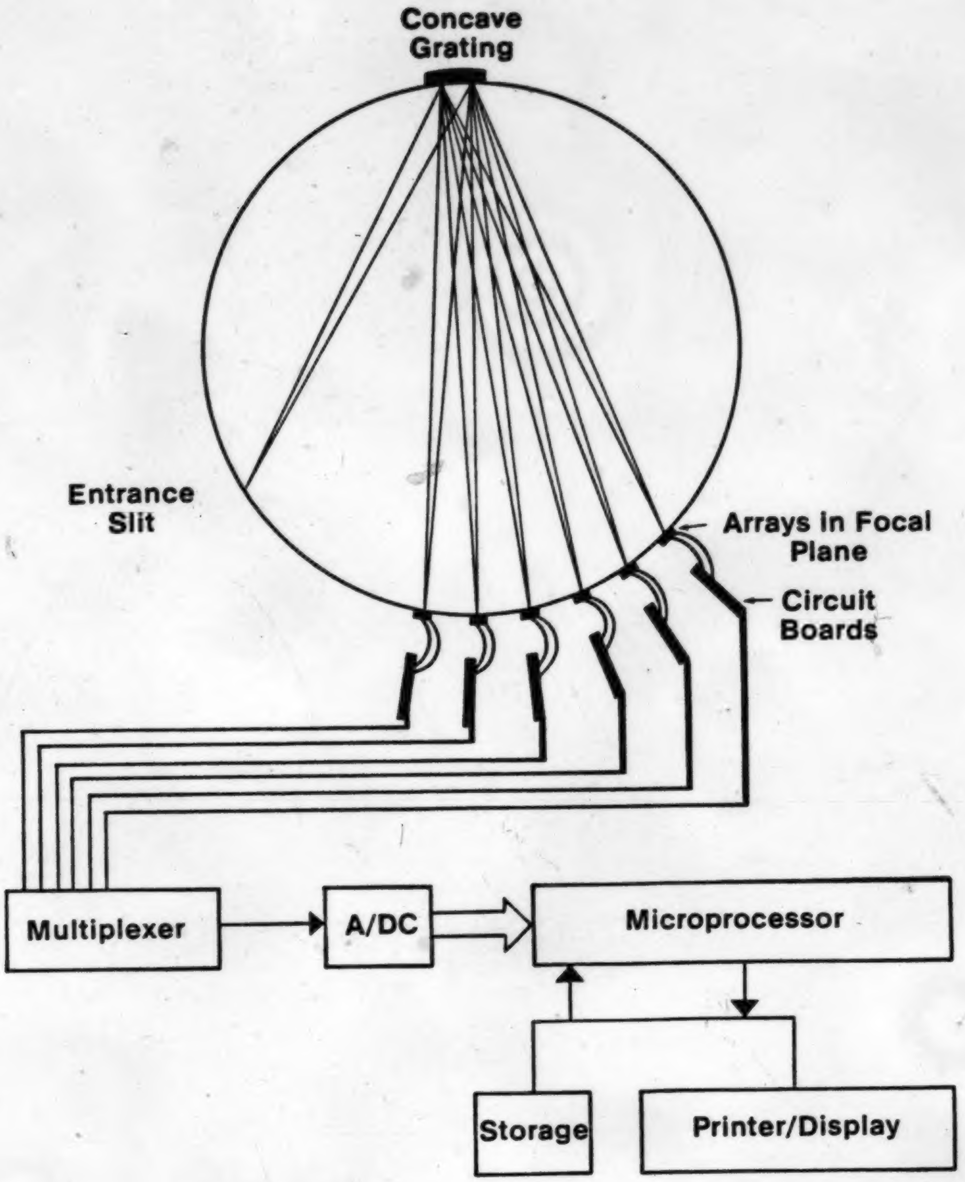
Concave Grating
Entrance Slit
Arrays in Focal Plane
Circuit Boards
Multiplexer
A/DC
Microprocessor
Storage
Printer/Display

Figure 2. A diode array based direct reader.

system, the secondary optics are discarded and short photodiode arrays placed directly in the focal plane. The diode arrays are positioned along the focal plane so that each one detects a spectral window which includes atomic emission of one, or more than one element. The arrays are mounted with the longest dimension of the diodes (height) parallel to the entrance slit images and each individual diode samples a different wavelength. The whole array thus gives spectral intensities over a wavelength window including the analyte signal and the neighbouring background.

Each diode array is individually controlled and its data output individually processed. In order to achieve versatility the diode arrays are capable of being moved anywhere on the direct reader focal plane subject to the restriction of their size and that of their immediate fittings.

The instrument can be adjusted to new applications quickly because the window of the photodiode arrays makes spectral line location fast and easy. Backgrounds can be measured directly in the same analytical determination as the analyte signals. Signals from different photodiode arrays can be interrelated to correct for direct spectral overlap. Once the arrays have been positioned, there are no moving parts to consider. Transient signals are measured as easily as steady signals.

This project covers the design and construction of such a system and its evaluation as a direct reading spectrometer.

CHAPTER II

THE BASIC COMPONENTS OF AN EXPERIMENTAL DIRECT READER

A direct reading spectrometer has the following basic parts.

1. A source of spectral information.
2. A system for dispersing light according to its wavelength.
3. A series of light detectors and transducers.
4. A data handling system.

1. The Source of Spectral Information

The main spectral source was an Inductively Coupled Argon Plasma (ICP) as described in Appendix 1. Analyte sample was introduced into the plasma using a glass concentric (Meinhard) nebulizer. Because the ICP was not always available, or desirable, three other spectral sources were occasionally used. These were:-

i. A Metrologic, MC 650, helium-neon laser, giving an intense spectral line at 632.8 nm.

ii. An Osram Spectralampe, cadmium discharge lamp.

iii. Several atomic absorption-type hollow cathode lamps.

2. The Light Dispersion System

The dispersion system was originally a Jarrel-Ash Company, Compact Atomcounter that had been designed prior to 1961. The original arc type spectral sources, the photomultiplier tube detectors and the measurement electronics were removed and discarded. The light-proof (dark) box was mounted on a steel frame so that the entrance slit was 51.5 cm above the floor. This was to make it compatible with available spectral sources that are mounted at that height. The following fittings are retained with the light-proof box:-

i. A 25 μm wide by 1.8 cm high fixed entrance slit with a sliding shutter mounted in front of it and a quartz refractor plate mounted behind it.

ii. A concave reflective diffraction grating 6.3 cm wide by 4.1 cm high with a radius of curvature of 1.5m. The grating has 1,180 grooves per mm and is blazed for 360 nm.

iii. The exit slit mounting rack in the approximate position of the focal plane of the direct reader and the photomultiplier tube mounting racks (Photographs 1 and 2). The exit slit mounting rack has a metric, steel measuring tape attached as a positioning guide.

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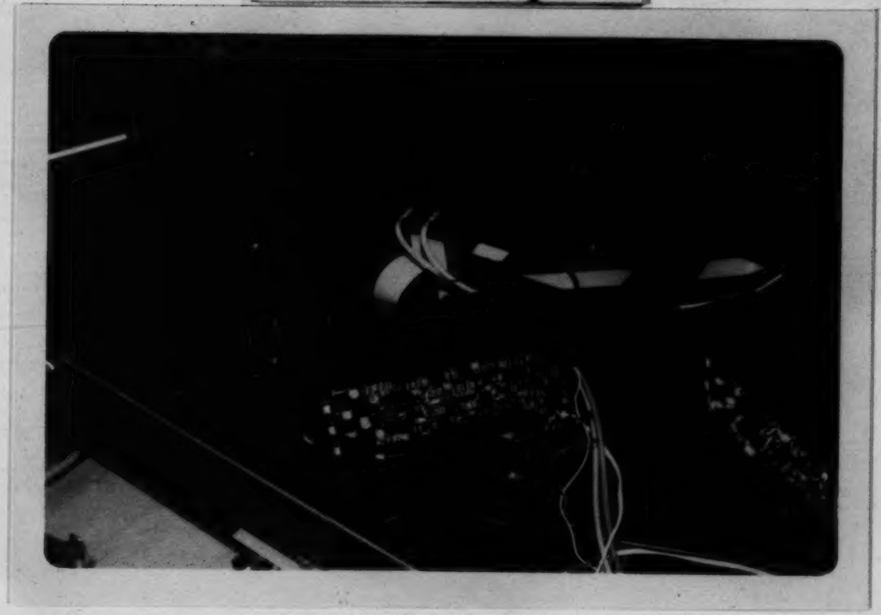


Photographs 1 and 2. The focal plane area of the direct reader.

The configuration is known as the Paschen-Runge mount and is based on the Rowland circle principle (Figures 1 and 2). This uses a concave reflective diffraction grating with a radius of curvature equal to the diameter of the Rowland circle. Thus the distance from the grating to the spectral focal plane opposite the grating is 1.5 m. Light from a point source on the circumference of the Rowland circle is dispersed and re-focussed by the concave grating to images along the circumference of the same circle [27,28]. It is a simple optical system as it does not require any optical devices within the instrument other than the single concave reflective grating. This allows full freedom in the placing of detectors.

The reciprocal dispersion is given by:-

$$\frac{d\lambda}{dl} = \frac{a \cos \beta}{nr}$$

where:- $\frac{d\lambda}{dl}$ = rate of change of light wavelength with change in position around the Rowland circle

a = grating ruling interval

n = spectral order

r = radius of curvature of the grating

β = angle of dispersion of a particular wavelength of light.

Hence our instrument has a reciprocal dispersion of 0.565 nm per mm directly opposite the grating and 0.540 nm per mm at an angle of dispersion of 17° (the limit of the useful arc of the instrument). The spectral range in first order is from 200 nm to 760 nm based on the geometry of the light-proof box.

3. The Light Detector and Transducer

3.1 Description

The Reticon "S" series self-scanning photodiode arrays provide individual sensor elements every 25 μm. When this is coupled with the dispersive system, the spectrum is sampled at 0.0135 nm to 0.0141 nm intervals. This is less than the width of the image of the entrance slit at the focal plane of the dispersive system. The "S" series arrays were specially developed for spectroscopic work having an aspect ratio of 100:1 (2.5 mm high by 25 μm spacing) so that they can sample large portions of the slit images in a spectrometer. Previous types of photodiode arrays were limited to a detector height of 0.6 mm [29].

Six 128 element arrays were obtained (RL128S). These were 2.72 cm long with a sensor width of 3.2 mm and were mounted as a standard 22 pin integrated circuit. Six evaluation circuits #RC1024S-1 were obtained to drive and handle the outputs for each array.

3.2 Mode of Operation

The diodes consist of bars of diffused p-type silicon semiconductor set in an n-type silicon substrate [30]. The whole detector is photosensitive. Light falling on a p-type semiconductor bar generates hole-electron pairs that directly affect the charge on that p-type bar. Light falling on the n-type semiconductor generates hole-electron pairs whose effect is shared by the adjacent p-type bars. The nearer p-type bar takes the larger portion (see Figure 3).

The diodes are operated in a storage mode. The p-n junctions are reverse biased, that is to say, the n-type substrate is held at a higher voltage than the p-type bars. In this mode the junction acts as a capacitor. During the reset procedure the p-type bars are grounded so that the capacitor becomes fully charged. The p-type bars are then isolated from ground for a period of time called the integration time.

Over this time period, the charge on the capacitor will be reduced by the reverse current flowing in the photodiode. This reverse current is due to both the photo-electrically generated current and to dark fixed pattern signal. At the end of the integration time, the p-type bars are connected to a previously grounded video line. The charge on the p-type bars divides between the

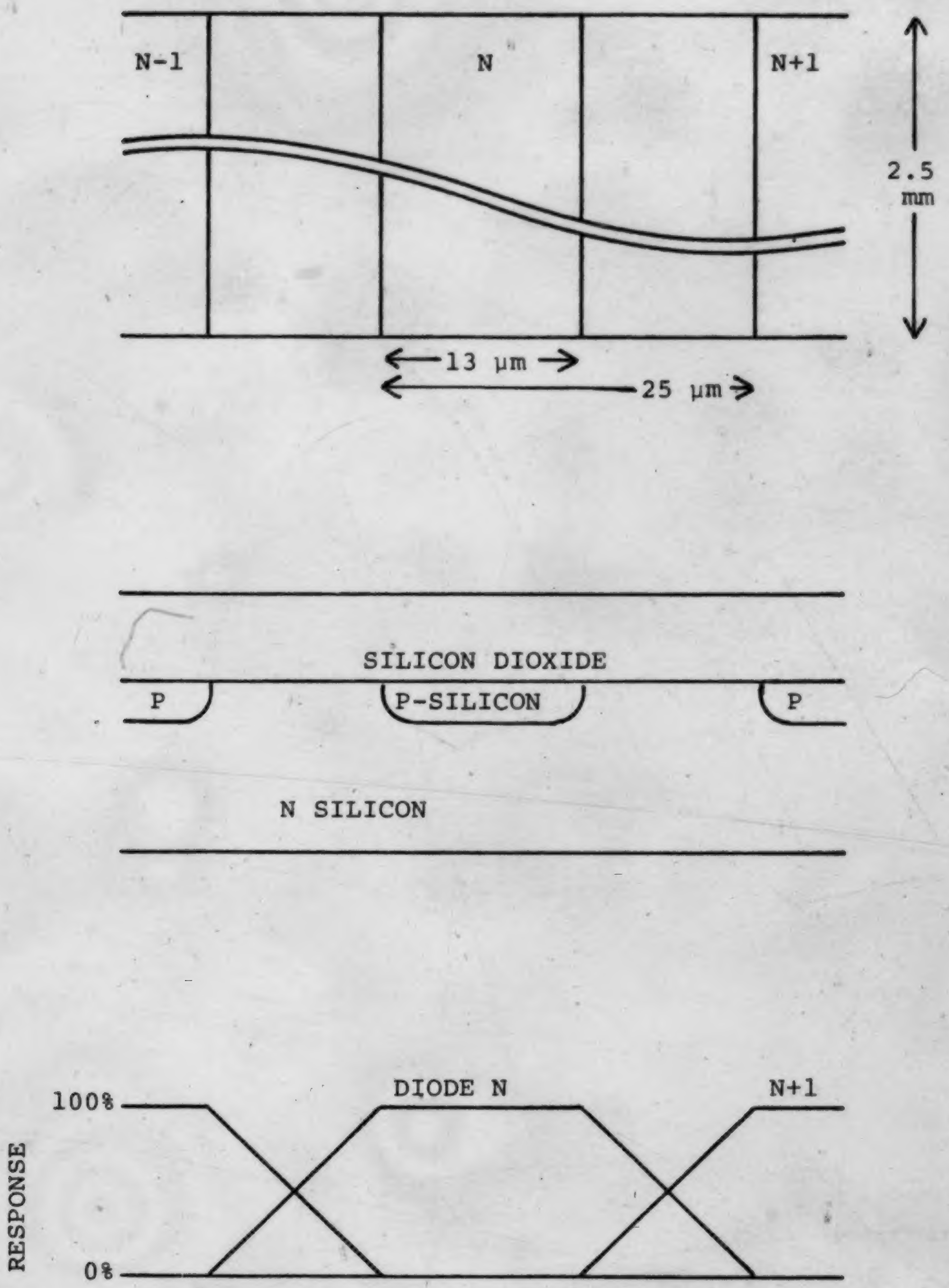

N-1
N
N+1
2.5 mm
13 µm
25 µm
SILICON DIOXIDE
P
P-SILICON
P
N SILICON
100%
DIODE N
N+1
RESPONSE
0%

Figure 3. Sensor geometry and response function of a photodiode array [30].

diode and the video line and the resulting change in the video line voltage is detected. As the n-type substrate is still held at the bias voltage (+5 Volts) the readout operation also recharges the capacitor for the next integration.

The full charge on the capacitance is 14 pC. When this has been fully discharged either by light or by the dark fixed pattern, the diode is termed saturated.

3.3 Spectral Response of the Array

The quantum efficiency of the photodiode in terms of hole-electron pairs generated per photon received is wavelength dependent with a maximum of 80% at 650 nm [30]. A plot of responsivity against wavelength is shown in Figure 4. Responsivity is the ratio of the charge lost at saturation to the saturation light exposure and has a maximum of 2.8×10^{-4} coulombs per joule per cm^2 at 750 nm. It decreases rapidly towards both the ultra-violet and the near infrared. The quantum efficiency curve would appear higher than the responsivity curve at lower wavelengths due to the higher energy of the lower wavelength photons. Recently data has been published [23] to show that the quantum efficiency decreases to a minimum of 35% at approximately 270 nm and then increases to a new maximum of 57% at 200 nm.

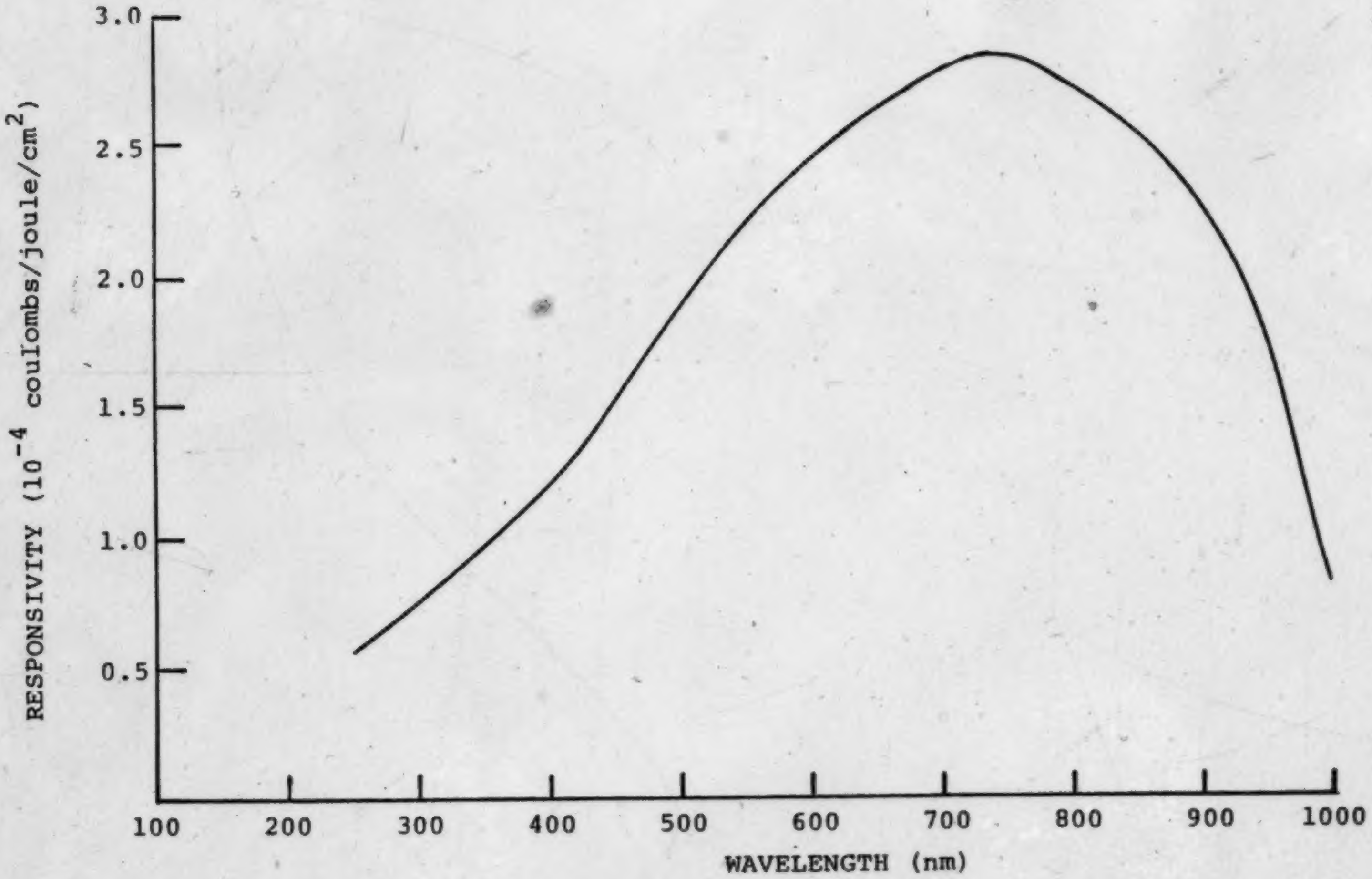


Figure 4. Typical spectral response of a photodiode array [30].

3.4 Readout

An equivalent circuit for the array switching system is given in Figure 5 [30]. Each cell consists of a photodiode and a dummy diode. Certain switching transients are capacitively coupled into the video lines. These same transients are introduced into the video lines of the dummy diodes and are eliminated by differential processing of the active and dummy video signals.

Scanning of the array during readout is controlled by two independent shift registers, one to address the odd numbered diodes and the other the even ones. Each shift register is driven by two phase clocks and scanning is initiated by a start pulse at the end of the integration time. The start pulse and the clock pulses are not generated on the diode array but are supplied and controlled by auxiliary devices. The use of separate switching and signal handling systems for odd and even diodes is a potential source of variability in the readout signal processing that has to be carefully controlled.

3.5 The Dark Fixed Pattern Signal

Dark fixed pattern signal decreases the charge on the diode capacitance and has two origins [31]: (i) the integrated dark current due to the thermal generation of hole-electron pairs and (ii) cross coupling between the

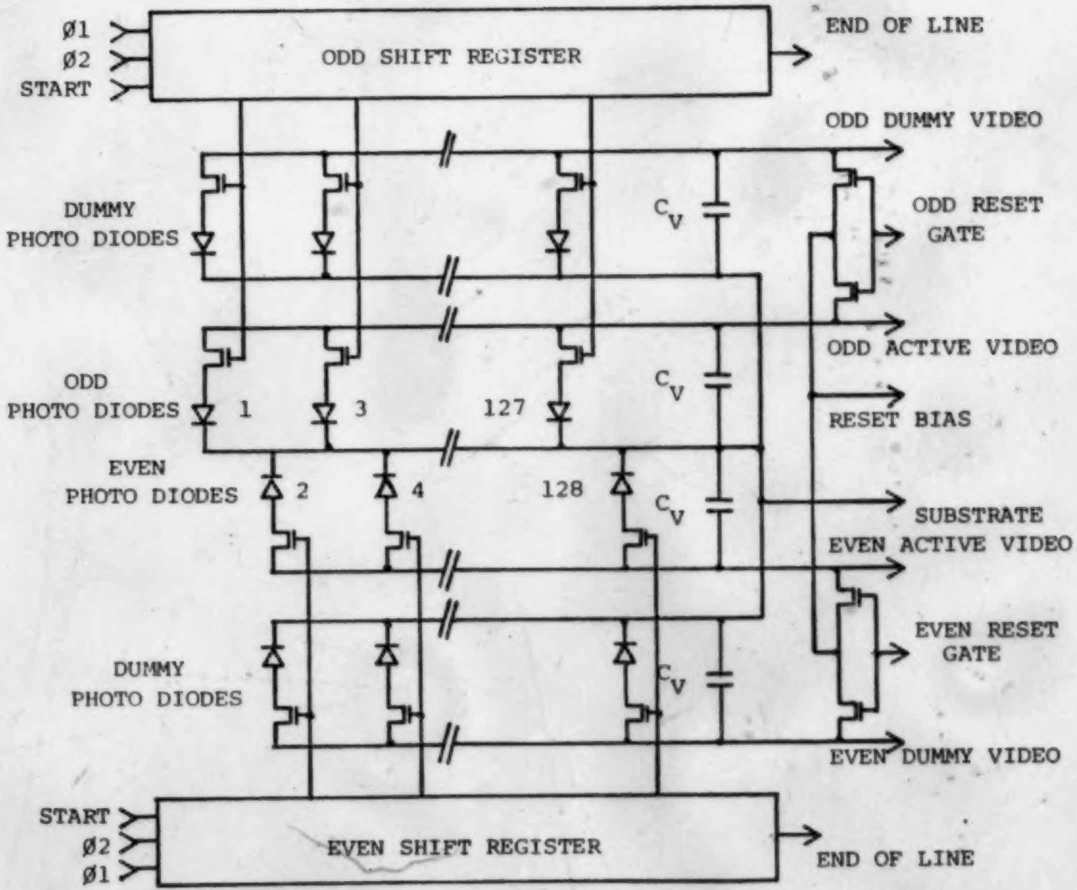

Ø1
Ø2
START
ODD SHIFT REGISTER
END OF LINE
ODD DUMMY VIDEO
DUMMY
PHOTO DIODES
ODD RESET
GATE
C_V
ODD ACTIVE VIDEO
ODD
PHOTO DIODES
1
3
127
RESET BIAS
EVEN
PHOTO DIODES
2
4
128
SUBSTRATE
EVEN ACTIVE VIDEO
DUMMY
PHOTO DIODES
EVEN RESET
GATE
EVEN DUMMY VIDEO
START
Ø2
Ø1
EVEN SHIFT REGISTER
END OF LINE

Figure 5. The equivalent circuit of the S series self scanning photodiode arrays [30].

video signal lines and the clock lines.

(i) In bulk silicon the density of thermally induced hole-electron pairs is given by [25]

$$n_T = 3.88 \times 10^{16} T^{3/2} \exp(-7015/T) \text{ per cm}^3$$

where T is the absolute temperature (K). The $T^{3/2}$ term covers the change with temperature of the density of allowable electron states in the conductance band of the semiconductor. It has little effect on the temperature dependency of the hole-electron pair production unless the array is operated at temperatures below -60°C [26].

At temperatures close to ambient, the exponential term is very significant. In practical terms, the dark current is halved for a 7°C drop in the operating temperature of the array. This is shown in Figure 6 [30].

In changing from photomultiplier tubes to photodiode arrays, the major loss is the approximately 10^6 times signal gain of the former. To partially compensate for this, the integration times of the photodiode arrays must be extended. In order to allow this, the signal due to the integrated dark current has to be reduced by cooling to prevent it from prematurely saturating the array.

(ii) The cross-coupling between the video signal and the various clock signal lines to the array is quoted in

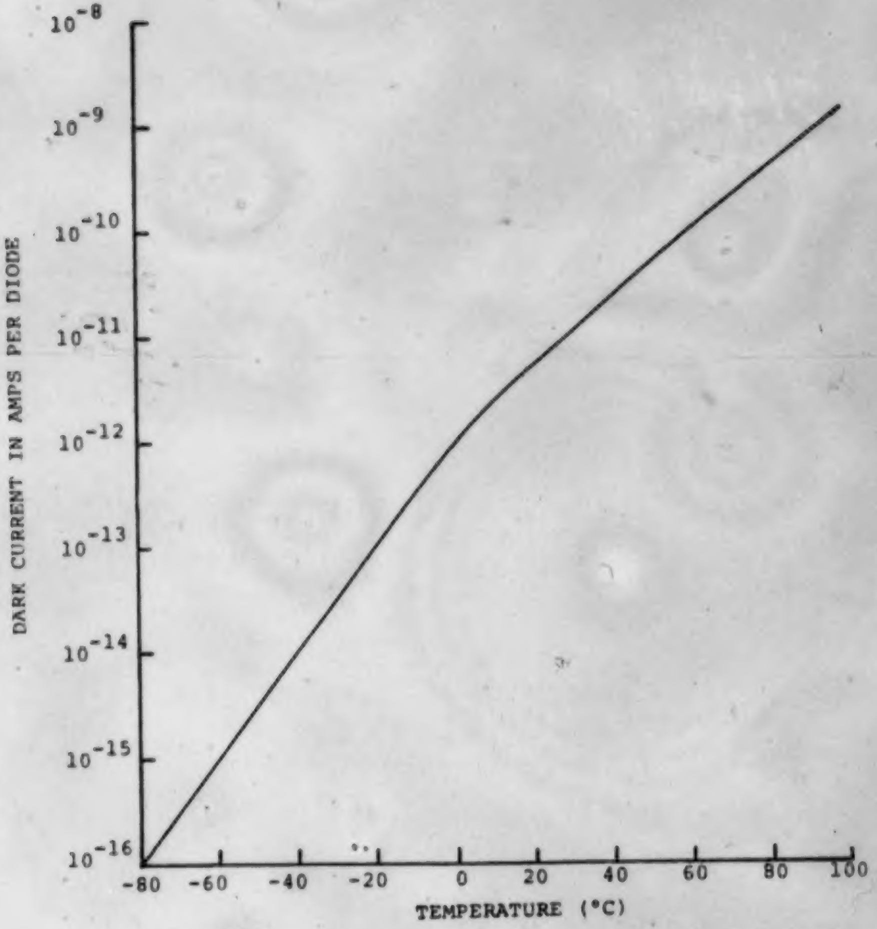


Figure 6. The temperature dependence of dark current [30].

the literature [23] as being of the order of 1% of the full-scale range of the diode array. Due to the physical restrictions placed on our system, this cross-coupling became a major factor that had to be controlled.

3.6 The RC1024S Printed Circuit Drive Board

The photodiode array is driven and its output processed by this circuit board which supplies the array with the following functions:-

i. Regulation and control of input drive voltages.

ii. An oscillator driven time base for the generation of all clock signals required for readout of the array and subsequent signal processing.

iii. An extension of the same time base through logic counters to generate the start pulse for readout after the integration time has elapsed.

iv. Synchronization of clock signal edges.

v. Conversion of the TTL based clocking signals to MOS levels to drive the array shift registers.

vi. Differential readout for active and dummy diodes for both odd and even sets of diodes.

vii. Further signal processing including combining the odd and even readout signals into a single chain of output signals.

viii. Supply and control of a DC restorative level against which all signal outputs are measured.

3.7 The Diode Array Mounting Carriage

The physical size of the RC1024S board (24 cm wide by 12 cm high) does not allow it to be considered as a direct carrier for the diode array in the focal plane of the direct reader. A carriage was built to carry the diode array in the focal plane. This clamps to the mounting rack that previously carried the exit slits (Photographs 1 and 2) where it can be moved to any position (see Figure 7).

The array position on the carriage can be adjusted to and from the centre of the Rowland circle for focussing purposes and vertically to allow the array to be positioned for receipt of maximum spectral line intensity. It has rotational adjustment about an axis along the normal to the Rowland circle to align the diodes with the images of the entrance slit in the direct reader focal plane. The whole carriage is kept aligned so that the array is tangential to the Rowland circle, by two steel pins that are held in contact with the edge of the mounting rack.

In addition to the array, the carriage carries a cooling system that reduces the working temperature of the array and hence the dark current.

The RC1024S circuit board is mounted close to the carriage, on a metal plate clamped to the racks that

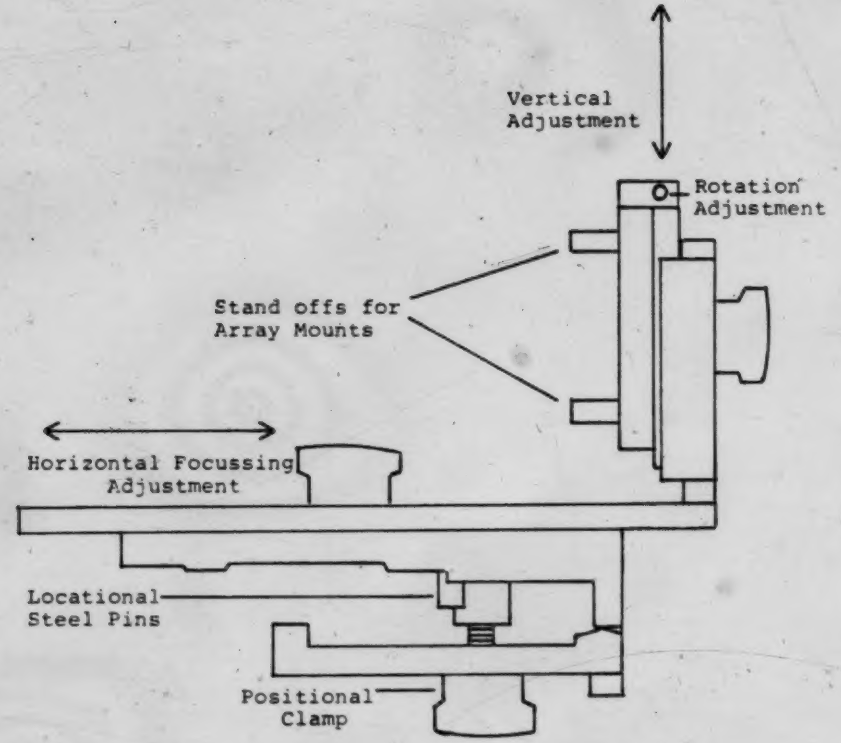

Vertical
Adjustment
Rotation
Adjustment
Stand offs for
Array Mounts
Horizontal Focussing
Adjustment
Locational
Steel Pins
Positional
Clamp

Figure 7. The diode array carriage.

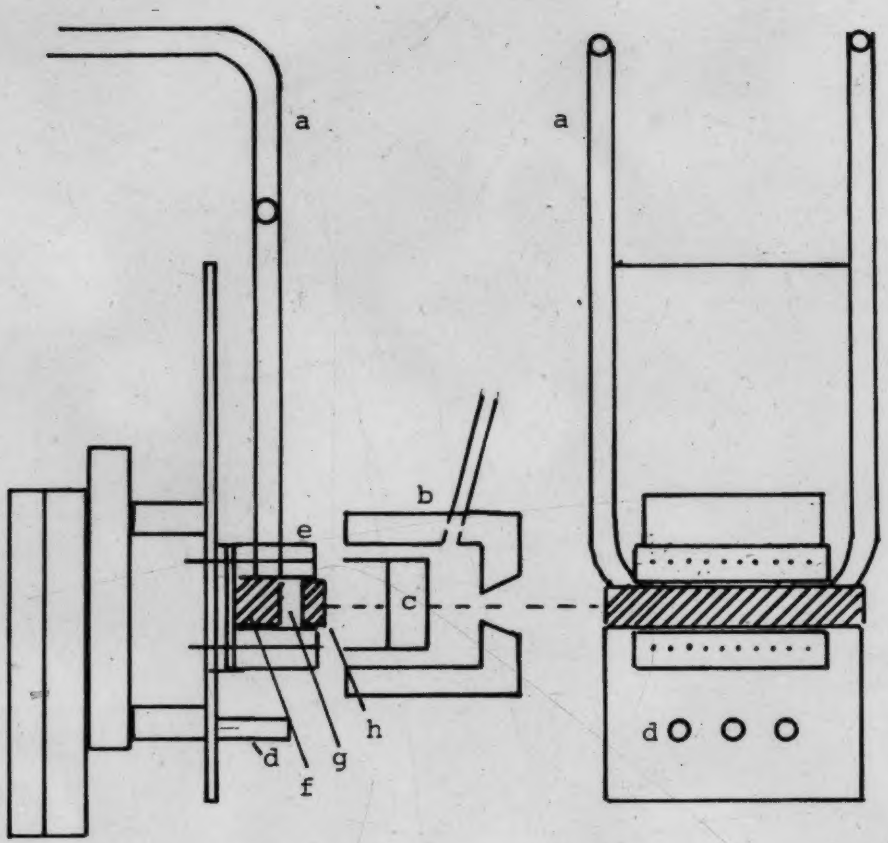
originally were used to mount the photomultiplier tubes (Photographs 1 and 2). The array is connected electrically to the RC1024S drive board by a 22 wire ribbon cable, 37 cm long, soldered to a socket on the array carriage and to a plug that fits into the RC1024S board socket.

3.8 Cooling Systems

In order to reduce the dark current, the arrays are cooled using thermoelectric (Peltier effect) heat pumps. Two types of coolers have been used.

(i) One, two or four miniature heat pumps, FC0.7-12-05L (MELCOR, Materials Electronic Products Corp., Trenton, NJ) are packed behind the array, between the two rows of electrical conductors in the 22 pin socket. The cold sides of the heat pumps are in contact with a copper bar that contacts the back of the array. The hot sides of the pumps are cooled by a water cooled copper heat sink (see Figure 8). Each of the miniature pumps is capable of transfering up to 1.56 watts.

(ii) A heat transfer bar is placed behind the array and connected to a copper plate mounted above the array. The copper plate is cooled by two CP1.4-71-06L Peltier effect heat pumps (MELCOR) which are themselves cooled by water cooled copper plates (see Figure 9). Each CP1.4-71-


a
a
b
e
c
d
f
g
h
d

a	cooling water feed
b	mask to control dry N_2
c	array
d	pins for attachment of heat pump wiring
e	socket
f	water cooled block
g	heat pumps
h	cooled copper block

FC 0.7-12-05L Heat Pump Actual Size

Figure 8. Array cooler based on miniature, Peltier effect, heat pumps.

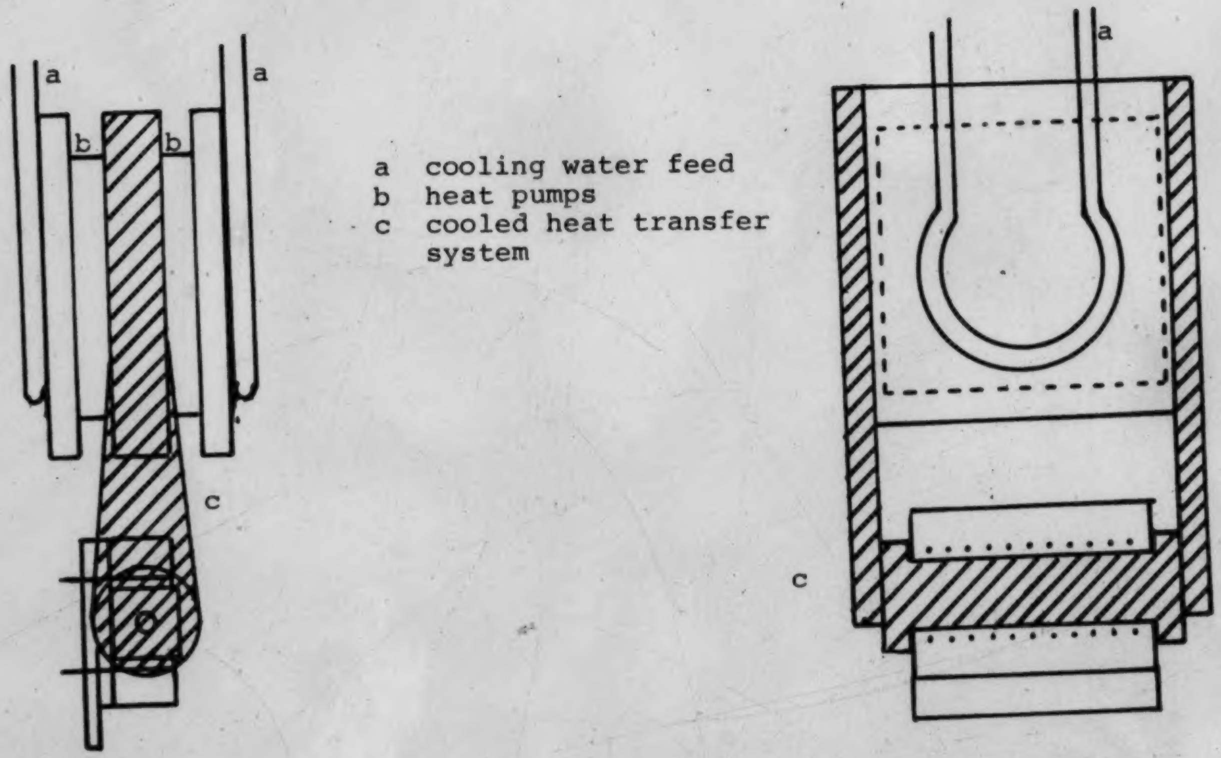

a
a
b
b
c
a cooling water feed
b heat pumps
c cooled heat transfer system
a
c

Figure 9. Array cooler based on larger, Peltier effect, heat pumps.

06L is capable of transferring 25 watts. These coolers can reach lower temperatures than the miniature pumps but they have to be carefully insulated to avoid water condensation and hence water saturation of the array socket.

All heat transfer surfaces are coated with a thin film of heat transfer paste supplied with the heat pumps.

A stream of low pressure (8-15 cm of water head) dry nitrogen is passed over the active portion of the cooled array to prevent the formation of an ice layer. The volume of nitrogen used is kept to a minimum by covering the array with a plastic mask that has a hole opposite the sensor portion of the array. These masks are made of black Delrin and partially shield the array against stray light.

4. Data Handling Systems

The following four data handling systems were used at various stages of this project:-

i. A transient recorder previously designed and built in our laboratory [33]. This had the capability of subtracting a recorded background from a signal. It could record a signal at a high sample rate (44 kHz) and later transfer that signal to an oscilloscope, effectively converting it into a storage oscilloscope.

The clocking rate of the recorder could then be reduced so that the data were fed out at a rate to match the pen response speed of a chart recorder.

ii. A PDP-8e minicomputer (Digital Electronics Corporation, Maynard, Mass.) fitted with a commercial 12 bit analog to digital converter. It was used at a sampling rate of 44 kHz. Like the transient recorder, it could subtract a recorded background from a signal and could support an oscilloscope and a chart recorder as outputs. It had the additional advantage of supplying data values in a printed form.

iii. An AIM 65 single board microcomputer (Rockwell International Corporation, Anaheim, California) interfaced with an ADC 1131J (Analog Devices, Norwood, Mass.) high speed 14 bit analog to digital converter. This was run at a sampling rate of 10 kHz.

iv. An Apple II+ microcomputer (Apple Computer Inc., Cupertino, California), interfaced with an AI13, 12 bit, 16 channel analog input system (Interactive Structures, Incorporated, Bala Cynwyd, Pennsylvania).

Both the AIM 65 and Apple based data processing systems were developed as part of this project and are described in more detail in Chapters IV and V.

CHAPTER III

PRELIMINARY EXPERIMENTATION

The RC1024S printed circuit boards, as supplied, would not drive the photodiode arrays in a manner suitable for use in a direct reader. Considerable modifications had to be made. This chapter describes why the modifications were necessary and how they were made.

1. Modification of the Oscillator

A photodiode does not have the high gain capability of a photomultiplier tube and its response has to be integrated over an extended time period in order to record low levels of light intensity.

All timing signals on the RC1024S board derive from an oscillator which had a frequency adjustable from 150 kHz to 1.5 MHz. The readout process at the end of the integration period is initiated by a start pulse. The timing chain for the generation of the start pulses consisted of four 4 bit, presettable binary counters in series. This gave a maximum of 65,536 counts before overflow corresponding to an integration time of 0.437 s when used to count a 150 kHz frequency. This was much too short for the direct reader. Additionally, during the readout process, diodes are sampled at every fourth cycle of the oscillator. This gave a minimum sampling rate of 37.5 kHz which is too fast for some data acquisition systems.

The oscillator is made from a Fairchild 9602 dual, retriggerable monostable multivibrator (see Figure 10). One monostable (B) runs as a fixed width pulse generator to give an output pulse width of approximately 100 ns. The other monostable (A) is used to generate the major portion of the oscillator period and its pulse width is controlled by a variable resistance.

The pulse width (time at high logic level) of the monostable is given by [34]

$$t_\omega = 0.31\ C_x R_x (1 + \frac{1}{R_x})$$

where t_ω is in ns, R_x in kΩ and C_x in pF.

The pulse width range of the variable monostable (A), where $R_x = R_2 + R_1$ (variable) and $C_x = C_1$, was altered by changing the capacitor C_1 from 500 pF to 0.005 μF. This changed the controllable frequency range of the oscillator to 16-260 kHz and the corresponding sampling rate to 4-62.5 kHz.

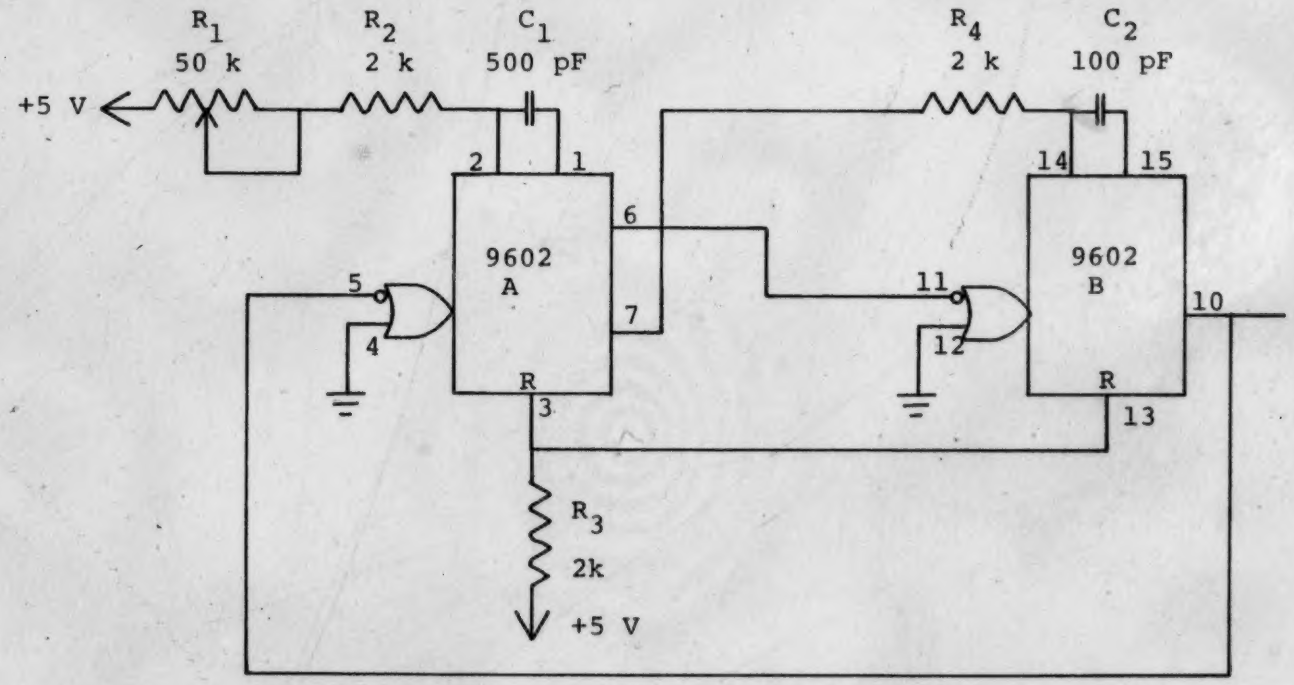

R_1
50 k
R_2
2 k
C_1
500 pF
R_4
2 k
C_2
100 pF
+5 V
2
1
14
15
6
7
9602
A
9602
B
5
4
11
12
10
R
3
R
13
R_3
2k
+5 V

Figure 10. The timing oscillator.

2. Extension of the Integration Timer

The oscillator modification suited the sampling rate but left the integration times still too short. This problem was corrected by increasing the timing chain from four to six 4-bit binary counters.

The last counter on the RC1024S board was removed and replaced by a DIP socket. Three more counters were mounted on a separate circuit board and connected to the RC1024S board by a plug-in ribbon connector (see Figure 11). This board was mounted parallel to and behind the RC1024S board. The three remaining counters on the RC1024S were set to full count. The counters on the extension board were connected through a ribbon cable to twelve switches mounted outside the dark box of the direct reader. The value of a bit on the extra counters could be added into the count by grounding its input control line with the corresponding switch. When the bit was not required in the count it was held at logic high by connecting to the +5 V supply through a 2.2 kΩ resistor.

The six 4 bit counters gave a maximum of 16.78×10^6 counts before overflow and, coupled with an oscillator set to give a 40 kHz sampling rate, allowed for integration times of up to 105 s.

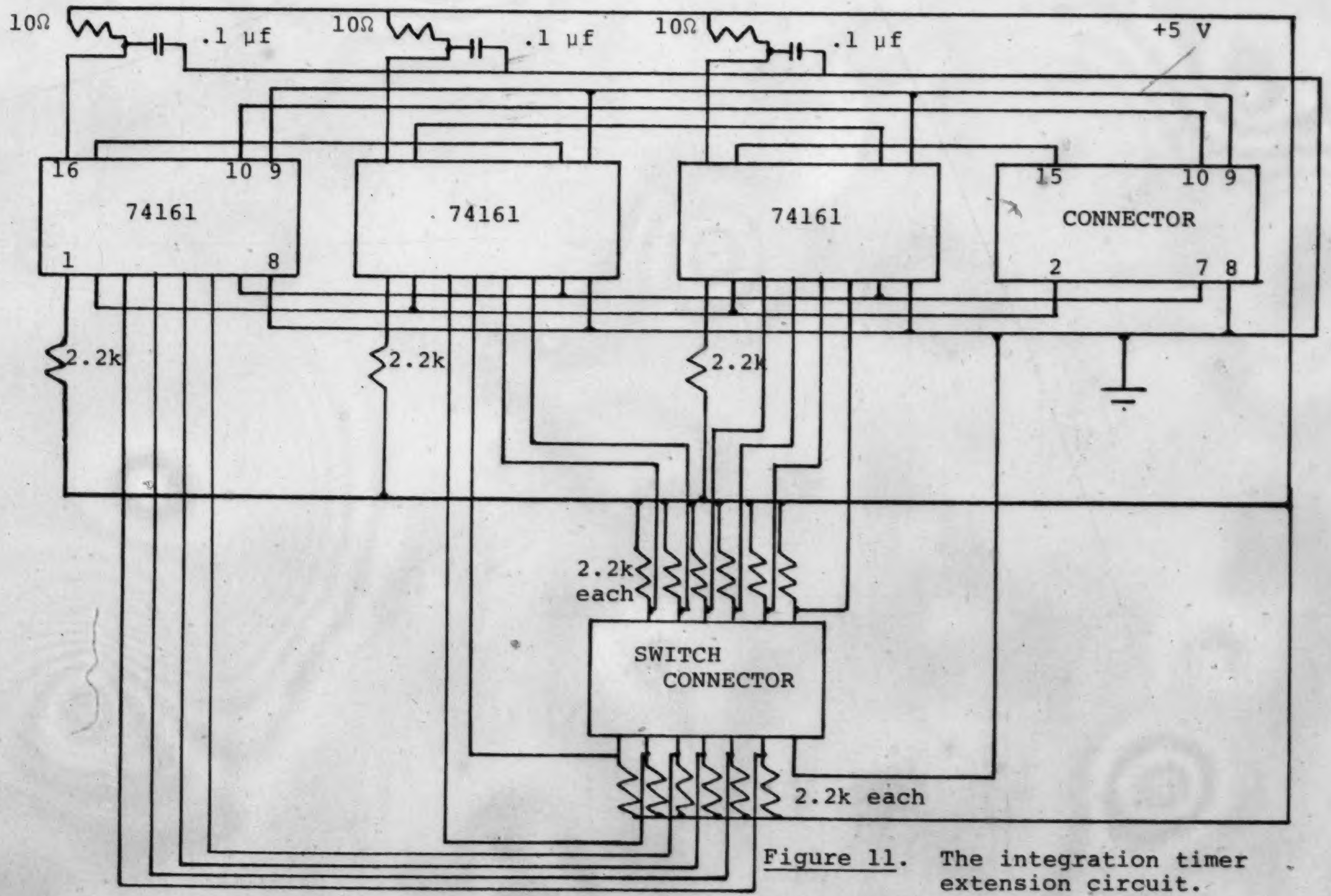

10Ω
.1 µf
10Ω
.1 µf
10Ω
.1 µf
+5 V
16
10 9
74161
1
8
74161
74161
15
10 9
CONNECTOR
2
7 8
2.2k
2.2k
2.2k
2.2k
each
SWITCH
CONNECTOR
2.2k each

Figure 11. The integration timer extension circuit.

3. A Data Acquisition Control Signal

A data acquisition system requires a control signal or trigger to initiate the collection and processing of a data value. The RC1024S board generates separate trains of sampling pulses for the odd and even series of diodes. At one point on the circuit board these are logically OR'd into one. This OR'd pulse train was picked up and connected to a spare edge connector tab on the circuit board. The widths of the pulses in this train were dependent on the frequency of the oscillator. This had to be changed so that the pulse width could be matched to the requirements of a subsequent data acquisition system.

It was also necessary to delay the data acquisition pulse so that the signal could be acquired when the signal output from the individual diodes was steady. The RC1024S circuit uses a differential readout of active and dummy diodes to minimize switching transients as the diodes are coupled, in turn, into the video output line. This is not so effective when the diode array is running remote from the RC1024S board and switching spikes appear in the array output signal.

A high speed data acquisition system contains an analog to digital converter. During the conversion the analog signal is held constant by a sample and hold amplifier. When such an amplifier switches from tracking the analog signal to hold, there is a small uncertainty in the time aperture during which the switching occurs. (Typically 0.5 to 1 ns with a fast acting device [35].) For accurate sampling, it is important that the signal to be converted does not change significantly during the switch to hold. Thus the analog signal from each diode must be sampled after the switching spike has passed.

Additionally, the signal may be preamplified both to take advantage of the full input range of the analog to digital converter and to have high frequency noise removed with a low pass filter. The damping effect of an amplifier will act on any sharp transitions in the analog signal (such as switching spikes) and further prolong their effect. For example, an array was sampled at 50 kHz or 20 μs per diode. Of this 20 μs, 5 μs was taken by the switching spike and a further 400 ns taken by the decay from the spike. A simple times three amplifier based on two CA3140 operational amplifiers caused the decay time from the spike to increase to 2 μs giving a total of 7 μs of disturbance in the 20 μs signal.

The data acquisition pulses were both delayed and their active widths made independent of the oscillator by the circuit, given in Figure 12, based on two 74121 monostable devices. The output of the delay monostable (A) goes to logic high on receipt of a negative transition

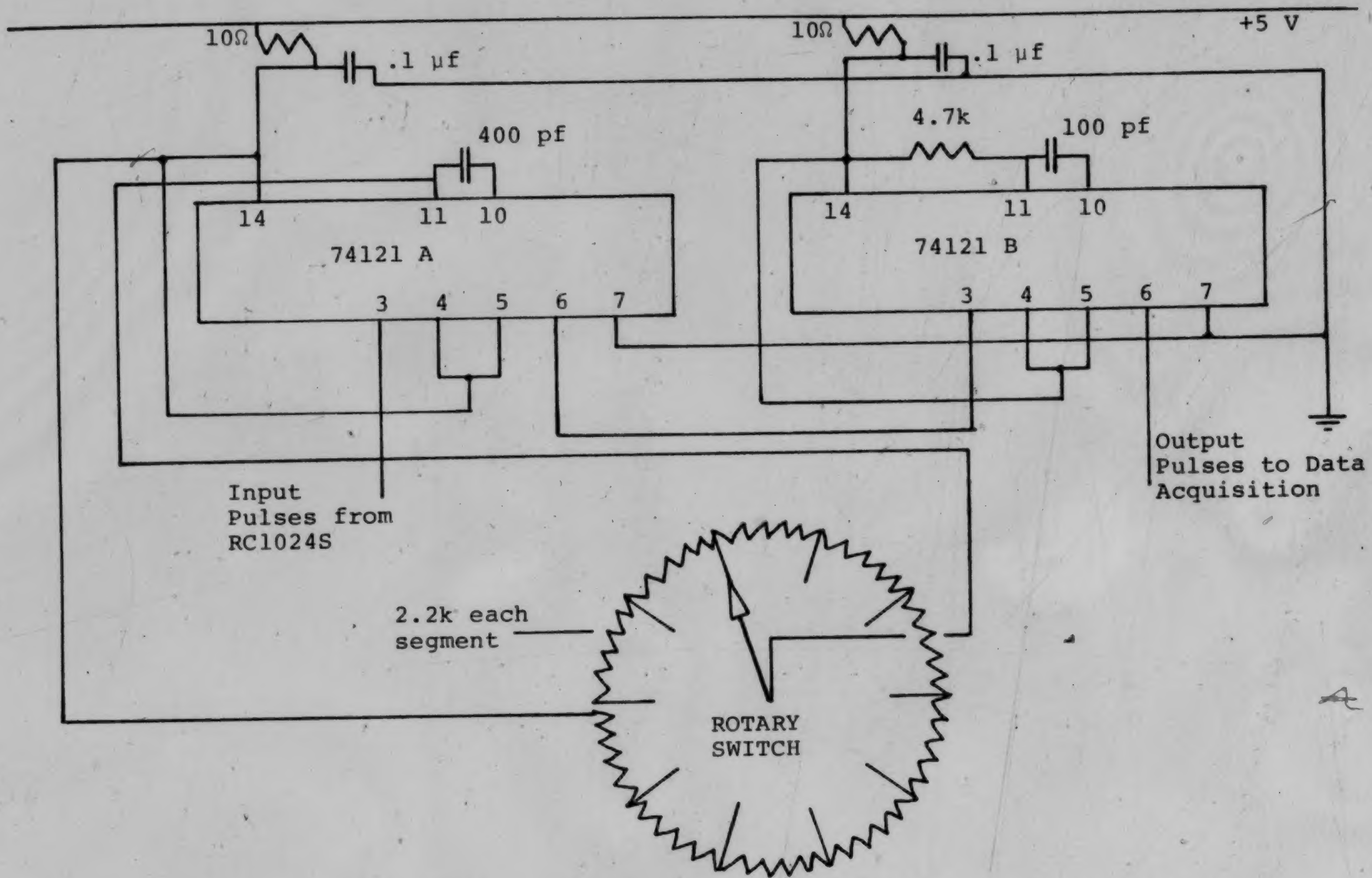

+5 V
10Ω
.1 µf
10Ω
.1 µf
400 pf
4.7k
100 pf
14
11
10
74121 A
3
4
5
6
7
14
11
10
74121 B
3
4
5
6
7
Input
Pulses from
RC1024S
Output
Pulses to Data
Acquisition
2.2k each
segment
ROTARY
SWITCH

Figure 12. The data acquisition control signal circuit.

from the RC1024S board. Its pulse width is controlled by the value of the timing capacitor (400 pF) and the switched-in timing resistors.

At the end of the controlled pulse width, the output goes low and triggers the start of the high level pulse on the pulse width control monostable (B). The output of the second monostable is used to signal the data acquisition system. The circuit shown in Figure 12 delayed the pulse from 5 to 10 μs and gave a pulse width of 400 ns. This version used a bank of fixed value resistors and a rotary switch to get repeatable delays for test purposes. Subsequent versions of this circuit used miniature trimming resistors on both monostables to give fine control of both the delay and pulse widths.

4. Signal Reduction Due to Extension

With the photodiode array plugged directly into the RC1024S circuit board, the signal from a fully saturated diode was approximately 3 volts. When mounted on the carriage away from the board, the signal value was only 1 volt.

This was investigated and it was found that separating the diode array from the circuit board by very small distances affected the signal value. Spare sockets were interposed between the array and the board and it was found that 8 sockets corresponding to a stand off distance of 4 cm reduced the signal by 20%.

When using the extension, the ribbon cable, socket and plug are between the array and its first amplifier stage (the differential amplifier). The readout mechanism for the photodiodes involves the sharing of charge between the diode and the video line. 28AWG ribbon cable has a capacity per line of 17.5 pF for a 38 cm length; well in excess of the 2 pF capacitance of each photodiode and the 3 pF capacitance of the array video line. Consequently the input voltage at the first amplifier stage is much reduced and this reduction continues through all subsequent amplifier stages.

Although the signal is reduced, it is still at an acceptable level and can be readily processed through external operational amplifiers to suit a data acquisition system.

5. Rapid Saturation of the Photodiodes

When a photodiode array was operated in extension, away from the board, it rapidly saturated with dark fixed pattern signal. This is illustrated in Figure 13 for the room temperature measurement of the 632.8 nm output of a helium-neon laser (highly filtered). The background increased rapidly, especially on the left side of the

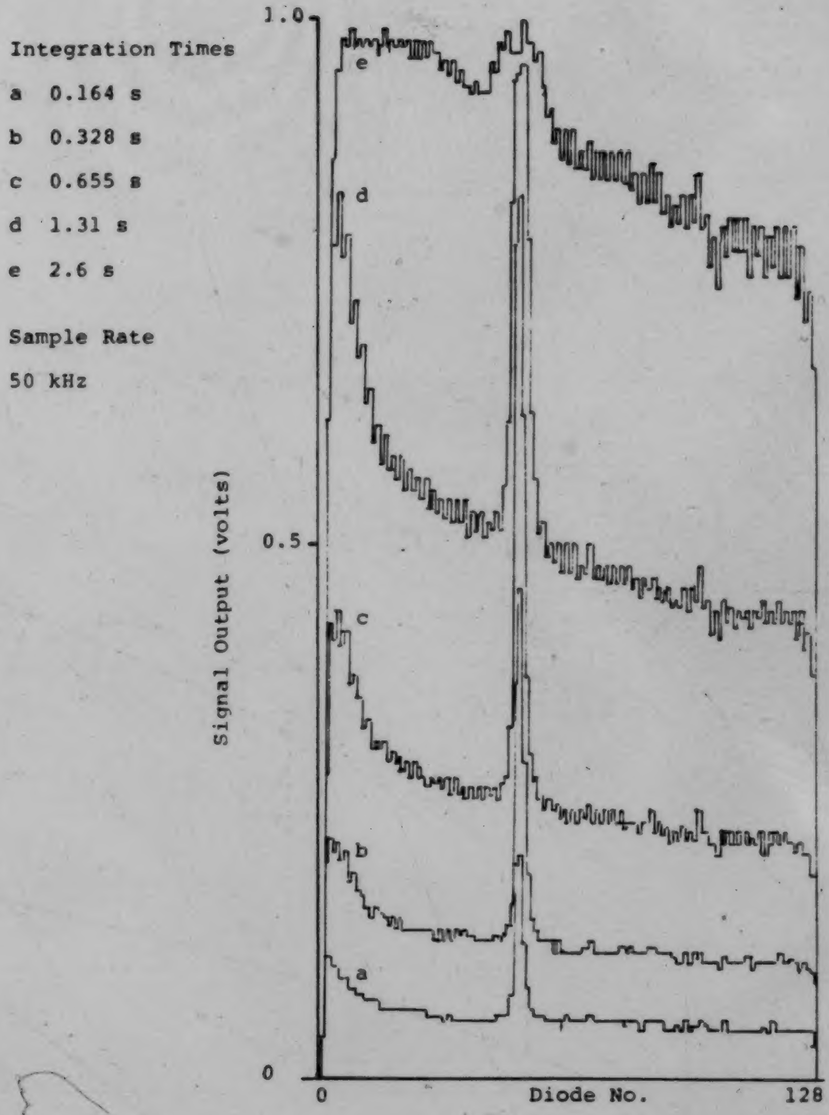


Figure 13. The rapid saturation of a diode array.

array where saturation started to occur at 1.6 s. The whole array would have been saturated by background in 3.2 s. This did not occur when the array was plugged directly into the RC1024S circuit board.

A cooling system (Figure 8) based on 2 miniature Peltier effect heat pumps was fitted to the array in extension. With a sampling rate of 43.5 kHz and 0.9 s integration time the effect of the cooler on this background signal was found to be minimal. It dropped the background level about 2% on the left side of the array and about 20% on the right side of the array. Because the efficacy of the miniature Peltier coolers was in doubt, the more powerful cooling system (Figure 9) was used. Again the background dropped very little on the left side of the array and by only about 50% on the right side. As the temperature of the array was measured as -27°C, a drop of 47°C below the temperature of the room, it was obvious that the background was not thermal in origin.

6. Investigation of the Background Effect

The internal temperature of the diode array integrated circuit was estimated by taking the mean of the temperature measured by two thermocouples, one in front of the array, the other between the array and the cold bar of the cooler. The difference between these 2 measurements was a maximum of 7°C at the extremes of the temperature ranges measured. The array temperature was varied over the range 261 to 340 K (-22 to 67°C) by controlling the voltage applied to the heat pumps. Temperatures above ambient were obtained by reversing the voltage across the pumps and so driving them in reverse. The array output signal was preamplified to give 10 volts at saturation.

For each array temperature, the output signal was measured for the left and right sides of the array for several integration times. The natural logarithms of the values were plotted against temperature for 2 integration times (Figure 14).

A similar plot developed from the formula for thermally induced hole-electron pairs [26]

$$n_T = 3.88\ (10^{16})\ T^{3/2}\ \exp(-7015/T) \text{ per cm}^3$$

would be almost linear but deviating towards the abscissa at lower temperatures. None of the curves on Figure 14 corresponded to this. The nearest was for the right side of the array at the lower integration time. The curves were interpreted as follows.

The background signal contained at least 2 components. One was the temperature and time dependent result of the generation of hole-electron pairs. The

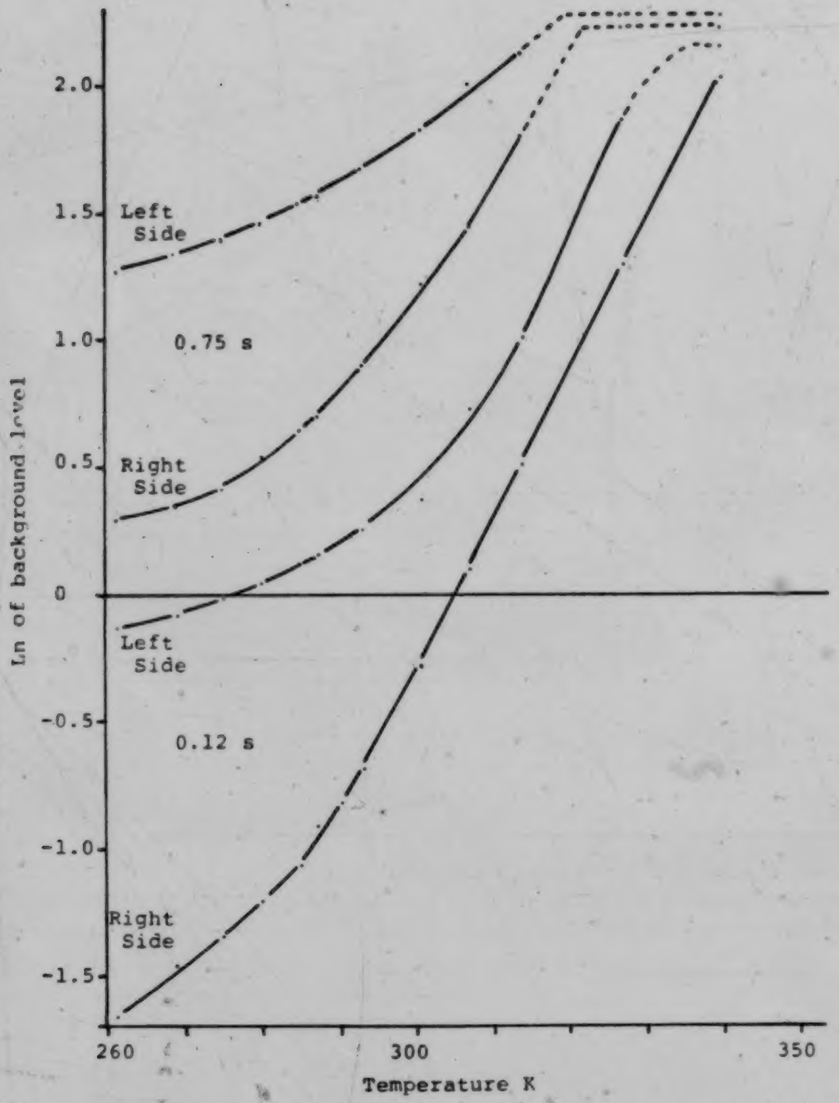


Figure 14. Variation of background signal with temperature for 2 integration times.

other was a time dependent but probably temperature independent background signal which was stronger on the left side of the array than on the right.

Because it diminished across the array, the time dependent, temperature independent background must have been either a function of distance from some fixed spot in the array or a function of time during the readout process taking the start pulse as the time origin.

The integration time was the product of the oscillator period and the count preset on the timing chain.

The oscillator frequency was changed and the counter setting altered to compensate and maintain the same integration times. The effect of making such changes on the background level on the right side of the array at room temperature are shown in Table 1. This shows that there was some dependence of background on the sampling rate. This was further investigated by cooling the array to -27°C. At these relatively short integration times, the time integrated dark current at -27°C should be insignificant so that background would be due to the temperature independent effect (Table 2).

Comparison of Table 2 with Table 1 shows that the background levels were reduced by reducing the thermal dark current and there was a direct relationship appearing

Table 1. Effect of changing sampling rate on background level at room temperature.

Sampling Frequency	Signal (Volts. 10 = Saturated) at integrations of				
= $\frac{\text{Oscillator}}{4}$	0.0942 s	0.1884 s	0.377 s	0.754 s	1.51 s
87 kHz	0.5	1.15	2.4	4.85	-
43.5 kHz	0.27	0.68	1.45	2.95	-
21.7 kHz	0.17	0.4	0.90	1.9	3.7
10.9 kHz	-	0.2	0.66	1.45	3.0

Table 2. Effect of changing sampling rate on background level at -27°C.

Sampling Frequency = Oscillator / 4	Signal (Volts. 10 = Saturated) at integrations of				
	0.0942 s	0.1884 s	0.377 s	0.754 s	1.51 s
43.5 kHz	0.07	0.22	0.55	1.3	2.5
21.7 kHz	0.03	0.08	0.26	0.6	1.2
10.9 kHz	-	0.03	0.06	0.2	0.4

between sampling rate (or the oscillator frequency) and the background level. These results together with others are rearranged in Table 3.

Thus the temperature independent background was linearly related to the number of oscillator periods in the integration time.

7. Removal of the Background Effect

The oscillator, through the first 4 bit counter of the counter chain and a read only memory (ROM) integrated circuit, sent 6 pulse trains continuously to the array.

It was not known which of these pulse trains was responsible for the background problem but with the array in extension there was considerable crosstalk between the signals in the wires that make up the ribbon cable. For example, the start pulse line picked up a 0.35 V induced pulse every 16 oscillator pulses continuously over the full length of the integration time.

Although the pulse trains were sent continuously, they were only utilized by the array during the readout process, after a start pulse had been generated. The reason that they were sent continuously is that the same oscillator drove both the readout mechanism of the array and the integration timer chain (see Figure 15).

Table 3. Relationship between background level and the number of sample pulses per integration at -27°C.

	Signal (Volts) and Integration Times (s) and Sampling Pulse Counts							
	16,384 Counts		32,768 Counts		65,536 Counts		131,072 Counts	
kHz	SIG (V)	INT (s)	SIG (V)	INT (s)	SIG (V)	INT (s)	SIG (V)	INT (s)
43.5	0.55	.377	1.3	.753	2.5	1.51	5.4	3.01
21.75	0.6	.753	1.2	1.51	2.6	3.01	5.2	6.03
10.9	0.4	1.51	1.2	3..01	2.5	6.03	6.4	12.1

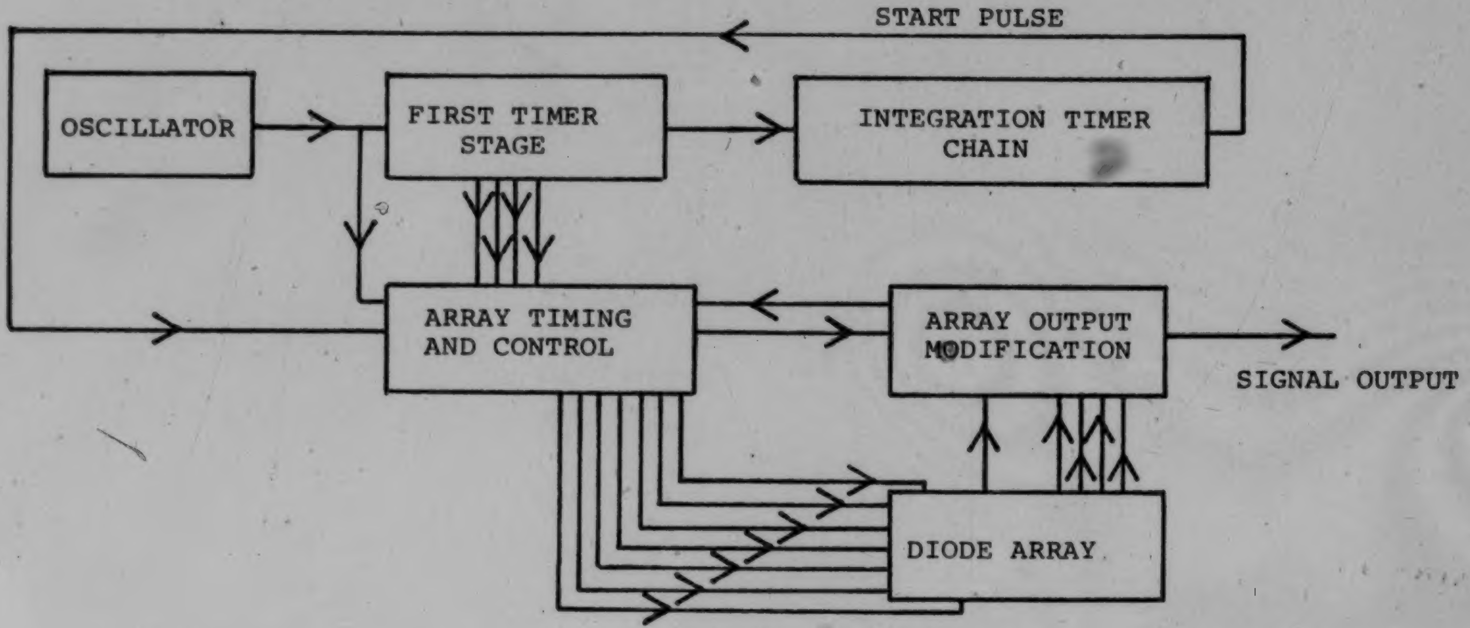

START PULSE
OSCILLATOR
FIRST TIMER STAGE
INTEGRATION TIMER CHAIN
ARRAY TIMING AND CONTROL
ARRAY OUTPUT MODIFICATION
SIGNAL OUTPUT
DIODE ARRAY

Figure 15. Schematic diagram of the RC1024 S array control system.

The alternative method of driving the array that solved the background problem is shown in Figure 16. The integration time is controlled by generating a start pulse away from the RC1024S circuit board. The oscillator is connected to the first timer stage, not directly, but through a logic gate. Although the oscillator runs continuously, it does not drive the system and hence send pulses to the array until the logic gate opens. The rising edge of the externally generated start pulse opens the gate and connects the oscillator to the timing chain and the array controls. The timing chain no longer controls the integration time but it is used to control the open time of the gate.

The timing chain is preset to allow 132 sample pulses to be generated and then its overflow pulse triggers the gate control to close the gate, after readout has been completed, and so re-isolate the oscillator from the rest of the circuit. Thus, regardless of the length of the integration time, the array receives only those pulses necessary for proper readout and is pulse free and consequently crosstalk free for the rest of the integration period. The timing sequence at the start of the readout cycle is shown in Figure 17. The externally generated start pulse goes high and opens the gate. At the same time it sends the output of a 7474 flip-flop on

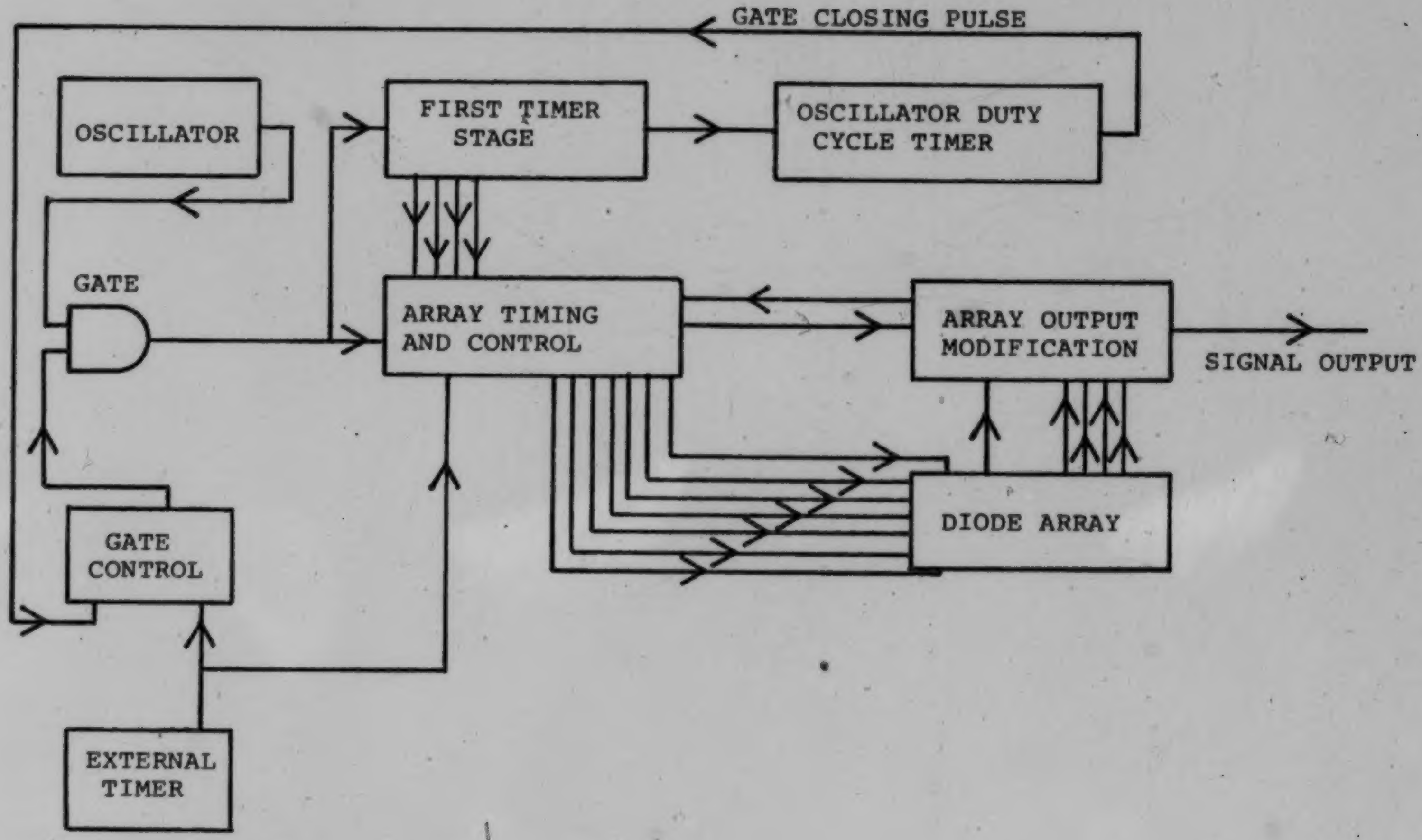

GATE CLOSING PULSE
OSCILLATOR
FIRST TIMER STAGE
OSCILLATOR DUTY CYCLE TIMER
GATE
ARRAY TIMING AND CONTROL
ARRAY OUTPUT MODIFICATION
SIGNAL OUTPUT
DIODE ARRAY
GATE CONTROL
EXTERNAL TIMER

Figure 16. Schematic diagram of the gated array control system.

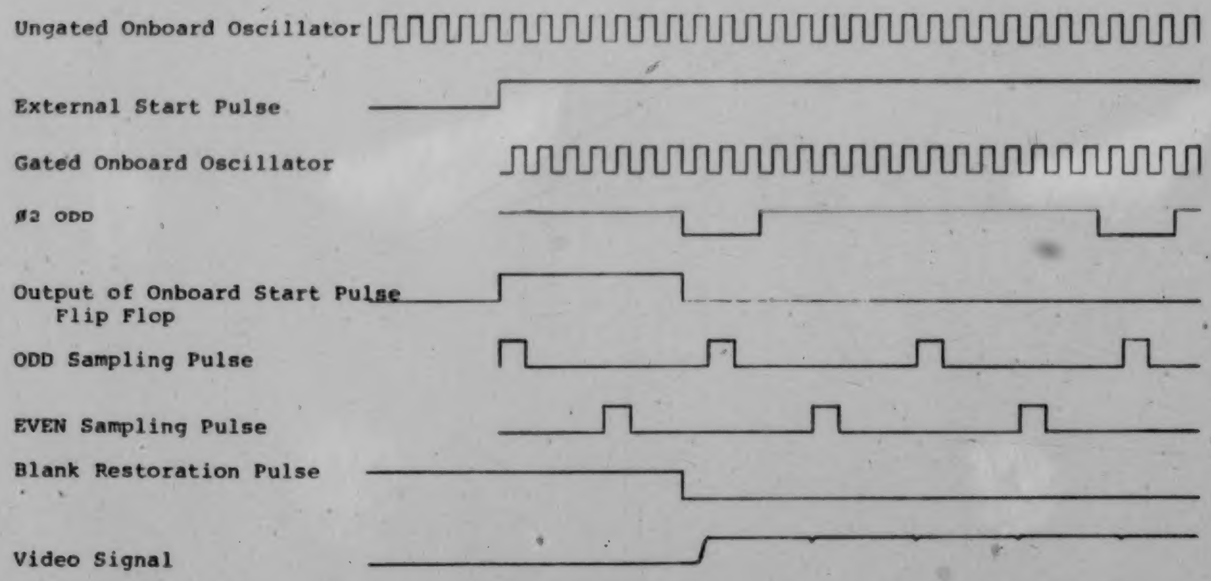

Ungated Onboard Oscillator
External Start Pulse
Gated Onboard Oscillator
ø2 ODD
Output of Onboard Start Pulse Flip Flop
ODD Sampling Pulse
EVEN Sampling Pulse
Blank Restoration Pulse
Video Signal

Figure 17. Timing diagram for the start of readout.

the RC1024S board high (see Figure 18). The oscillator is now connected to the control system which starts to generate its trains of timing pulses. As soon as one of them, called 02 ODD, goes low for the first time, it clears the onboard 7474 flip-flop (Figure 18), sending its output low. It is this high to low transition, inverted and converted to MOS logic levels by the MH0026, that acts as the true start pulse for the array. At the same time the complementary output of the 7474 flip-flop goes high and clocks a second 7474 flip-flop which, in turn, cuts off the blank restorative signal. The blank restorative signal is that signal that the board puts out when the array is not being read out.

The photodiode signal values are then processed by the RC1024S circuit board under the control of the sampling pulses. During the time that the start pulse 7474 flip-flop is high, two sampling pulses are generated. The software of the data handling system must be designed to ignore these first two pulses as they occur before the photodiode array readout has started. This is done by waiting for the negative edge of the flip-flop output to occur before taking data values.

The timing sequence at the end of readout is shown in Figure 19. As the last diode (number 128) is read out, the array sends out an end of line signal. This is fed to

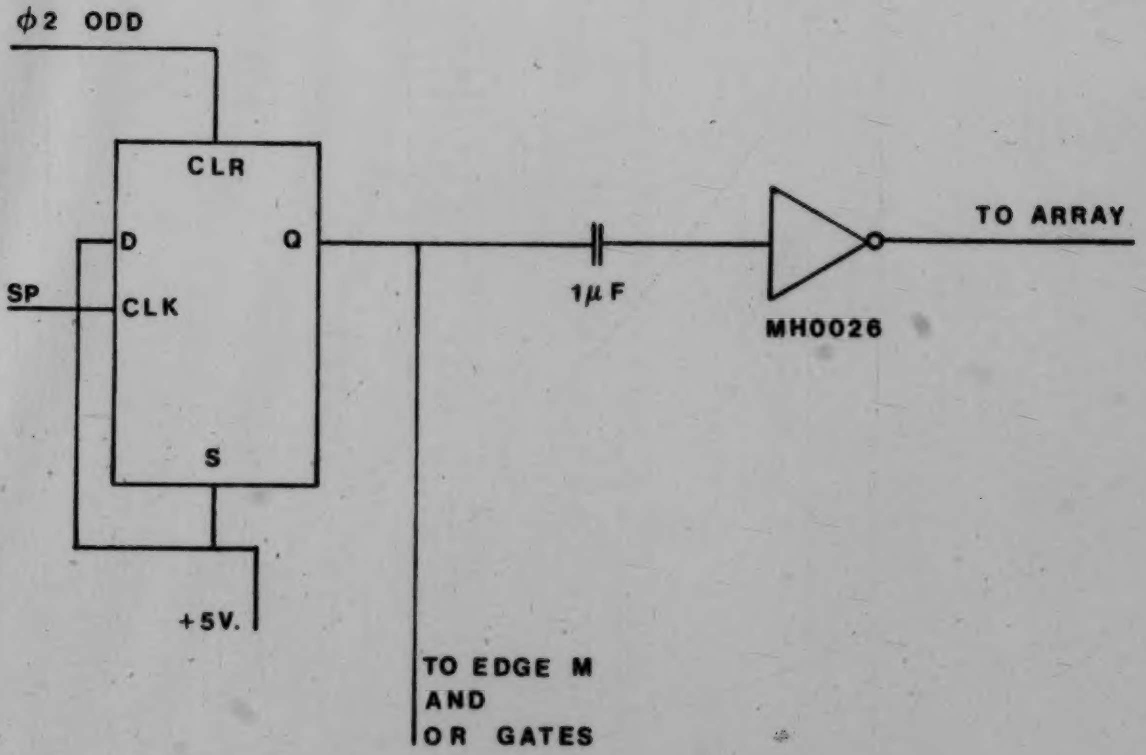

ϕ2 ODD
CLR
D
Q
SP
CLK
S
+5V.
1μF
MH0026
TO ARRAY
TO EDGE M
AND
OR GATES

Figure 18. The start pulse circuit on the RC1024S board.

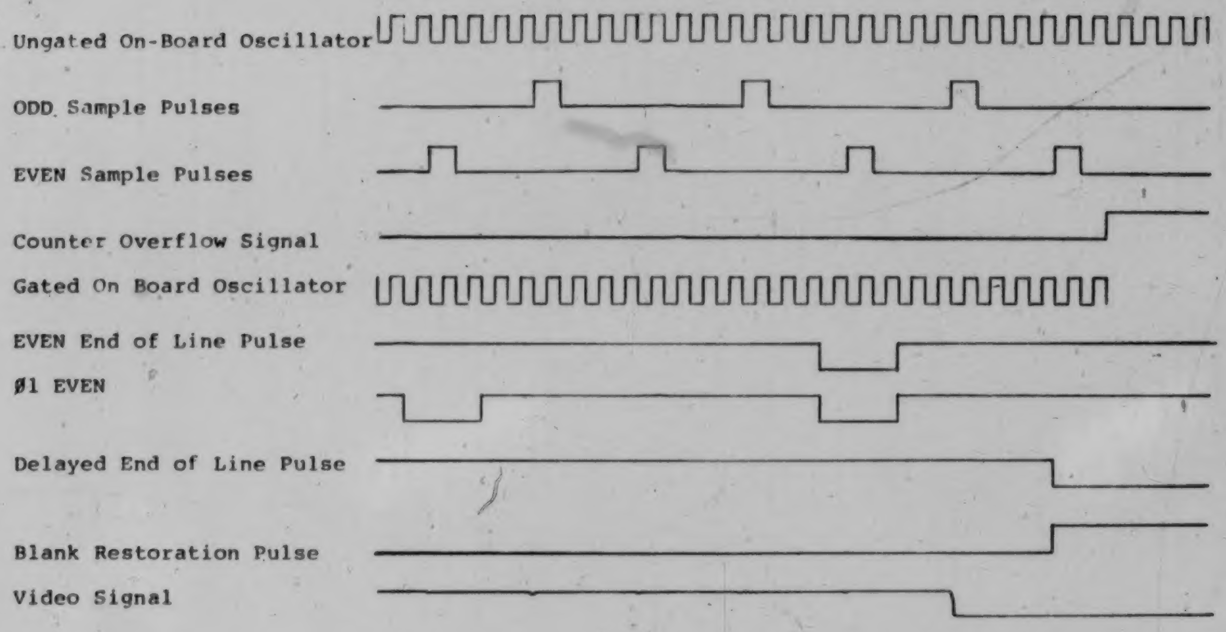

Ungated On-Board Oscillator
ODD Sample Pulses
EVEN Sample Pulses
Counter Overflow Signal
Gated On Board Oscillator
EVEN End of Line Pulse
Ø1 EVEN
Delayed End of Line Pulse
Blank Restoration Pulse
Video Signal

Figure 19. Timing diagram for the end of readout.

a shift register on the RC1024S board where it remains until the next even sample pulse is generated. This sample pulse clocks the shift register and, now delayed, clears the 7474 flip-flop controlling the blank restorative level, thus restoring that level. This takes a further 2 sample pulses so at least 132 sample pulses have to be generated to read out the array.

The external start pulse generator is shown in Figure 20. It consisted of a 9602 dual monostable generating approximately a square wave at a frequency of 1 kHz. Four 4 bit counters 74161 were used as a timing chain. The controlling inputs for the first counter were switched to ground for it to have a full count of 16. The controlling inputs for the remaining 3 counters were held high by connecting them to the +5 V supply through 2.2k resistors, but they could be grounded through a ribbon cable using switches outside the dark box of the direct reader. The overflow pulse from the counter chain was inverted to give a pulse to enable the reloading of the counters and then reinverted to give the required start pulse. The oscillator was tuned slightly so that the external switches controlled the integration time over the range of 15.6 ms to 64 s.

The gate consists of a dual edge triggered D type flip-flop 7474 and a quad NAND gate 7400 (Figure 21). The

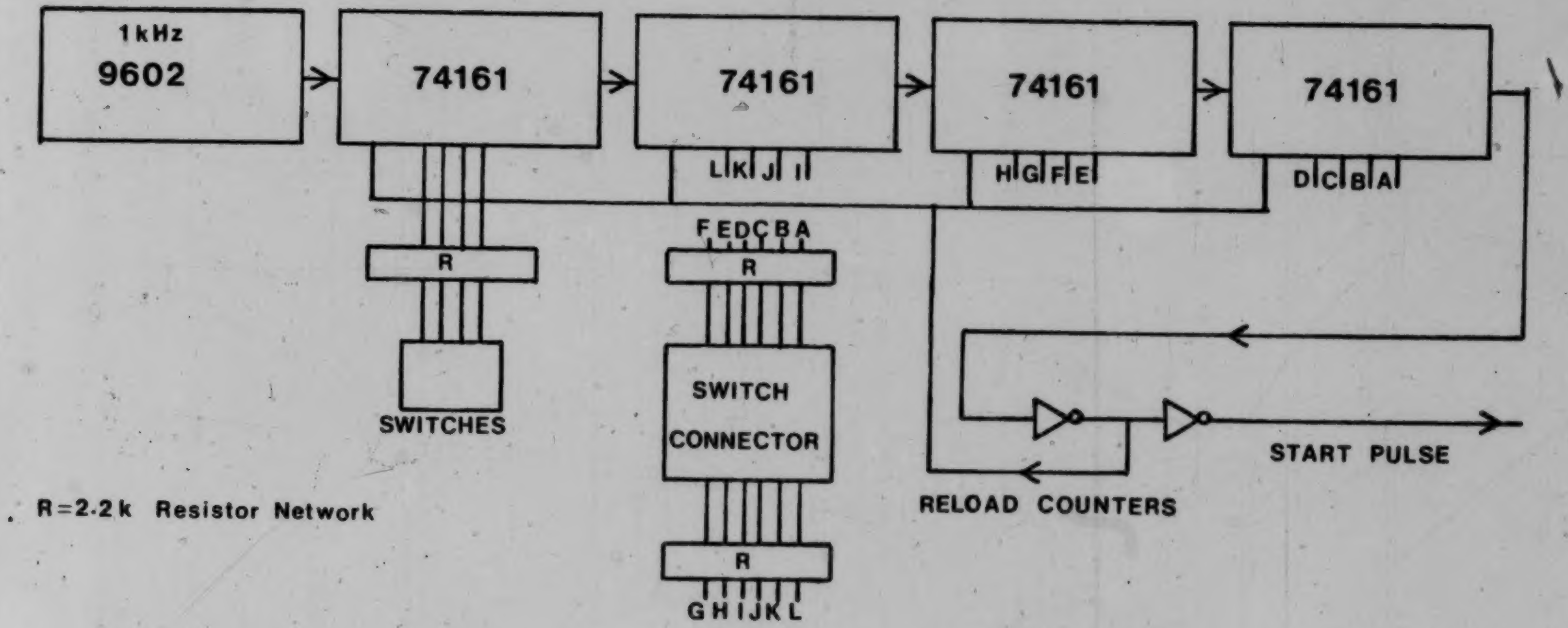

1kHz
9602
74161
74161
74161
74161
LKJI
HGFE
DCBA
R
SWITCHES
FEDCBA
R
SWITCH
CONNECTOR
R
GHIJKL
START PULSE
RELOAD COUNTERS
R=2.2k Resistor Network

Figure 20. The external start pulse generator.

(This is the external timer in Figure 16.)

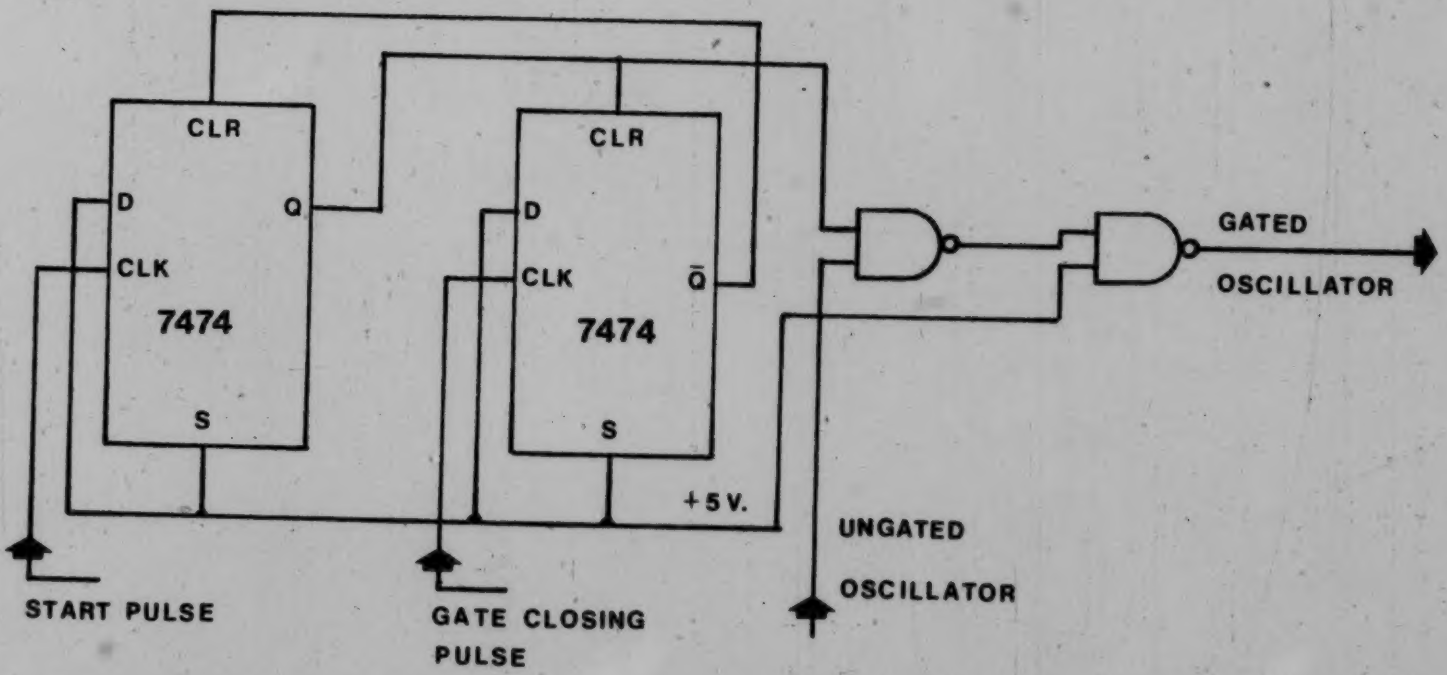

CLR
D
CLK
Q
7474
S
CLR
D
CLK
Q̄
7474
S
+5 V.
START PULSE
GATE CLOSING PULSE
UNGATED OSCILLATOR
GATED OSCILLATOR

Figure 21. The oscillator gating circuit.

(This is the gate control and gate in Figure 16.)

D and S inputs of both flip-flops are locked high. In this mode the output of each flip-flop goes high on the first rising edge received at the clock input, whether the rising edge is the leading or trailing edge of a pulse.

The Q output of the first flip-flop is the gate control. It goes high and opens the gate when the flip-flop is clocked by the rising edge of the externally generated start pulse. When readout has been completed the overflow pulse from the RC1024S board clocks the second flip-flop sending its Q output high and its complementary $\overline{Q}$ output low. This $\overline{Q}$ output clears the first flip-flop which closes the gate and then clears the second flip-flop. The device is now ready for the next start pulse to occur.

The gate control level from the first 7474 flip-flop and the output of the oscillator from the RC1024S board are inputs to a 2-input NAND gate. When the gate control level is high the output from the NAND gate is the inverted oscillator signal. This is reinverted using a spare gate on the 7400 in the inverter mode.

The start pulse generator, the gate and the data acquisition control signal modification circuits were all mounted on a board attached behind the RC1024S board.

The alterations to the RC1024S board covered in this chapter are described in detail in Appendix 2.

Use of the gated oscillator method of running the array removed the temperature independent background problem. The integration time is now limited by the true dark current caused by the thermal generation of hole-electron pairs. This current did not saturate the photodiode array in 64 s (the limit of the integration timer system) at -2°C.

CHAPTER IV

A SINGLE ARRAY SYSTEM AND THE AIM 65 MICROCOMPUTER

A single array system was built as a precursor to the multiple array direct reader in order to gain experience with operating conditions, software design and data evaluation.

It was based on the use of the gated oscillator and the externally generated start pulse method of running an array as described in Chapter III. A data acquisition system was assembled based on the Rockwell AIM 65 single board microcomputer and a high speed, successive approximation, analog-to-digital converter. The system was used to determine the operating characteristics of the array and its response as a quantitative spectrophotometric detector.

1. Interfacing the Array to the Computer

The whole detector, data collection system involved the following components:-

i. The photodiode array.

ii. The array carriage and its ribbon cable.

iii. The array drive board RC1024S.

iv. The supplementary circuits to generate the start pulse, gate the oscillator and modify the data acquisition control pulses.

v. An analog multiplexer and preamplifier.

vi. An analog to digital converter complete with sample and hold amplifier.

vii. The AIM 65 computer.

The first four components have been described in previous chapters.

1.1 The Analog Multiplexer and Preamplifier

The circuit for this is drawn in Figure 22.

The HI-508A (Harris Corporation) is an eight channel CMOS analog multiplexer. Although not required in a single channel system, it was included because it, or a similar device, would be needed in a multiple array system. It was used here, permanently switched to input channel number 1 by grounding the input control lines.

The operational amplifiers used were TL081 (Texas Instruments), a high slew rate, JFET-input type. The first operational amplifier acted as a second order low pass filter (40 dB fall off per decade) with an adjustable 3 dB point in the 5-50 kHz range. The design came straight from a manufacturers handbook [36]. It also

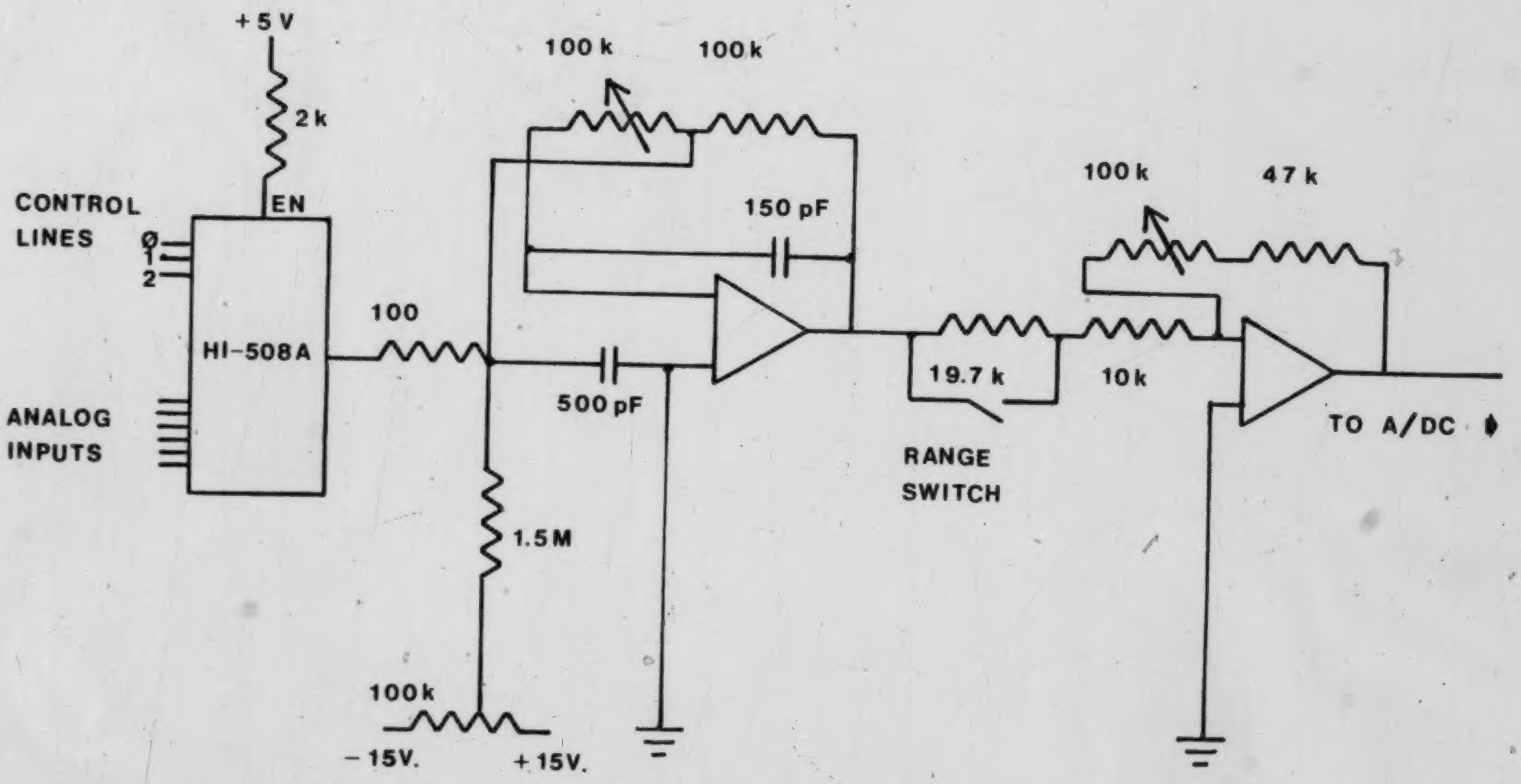

+5 V
2k
EN
CONTROL LINES
0
1
2
HI-508A
ANALOG INPUTS
100
100 k
100 k
150 pF
500 pF
1.5 M
100 k
−15V.
+15V.
19.7 k
RANGE SWITCH
100 k
47 k
10 k
TO A/DC

Figure 22. The pre-amplifier for the AIM 65 system.

inverted the signal and acted as a summing amplifier to allow the incoming signal to be offset by ±1 volts. The low pass filter was included to exclude noise from exterior sources such as the inductively coupled plasma radiofrequency power supply. The second operational amplifier reinverted the signal and amplified it by 4.7 to 15 times so that the array signal could be expanded to match the full range of the analog to digital converter. The high-low range switch was added to allow a divide by 3 operation without disturbing the gain control settings on the amplifier.

1.2 The Analog to Digital Converter

Standard commercial devices were used. The converter was an ADC 1131J by Analog Devices, which gave a 14-bit conversion in 12 μs. During the conversion the analog signal was held constant by a sample and hold amplifier SHA 1144. Both components were mounted on a circuit board (AC 1580) from the same supplier. Jumpers were set on the AC 1580 board to set the full range of the converter to 0-10 volts and to put the switching of the sample and hold device under the control of the $\overline{\text{STATUS}}$ output of the converter. The A/DC contained its own internal clock for control of the conversion. The timing diagram for the conversion is given in Figure 23.

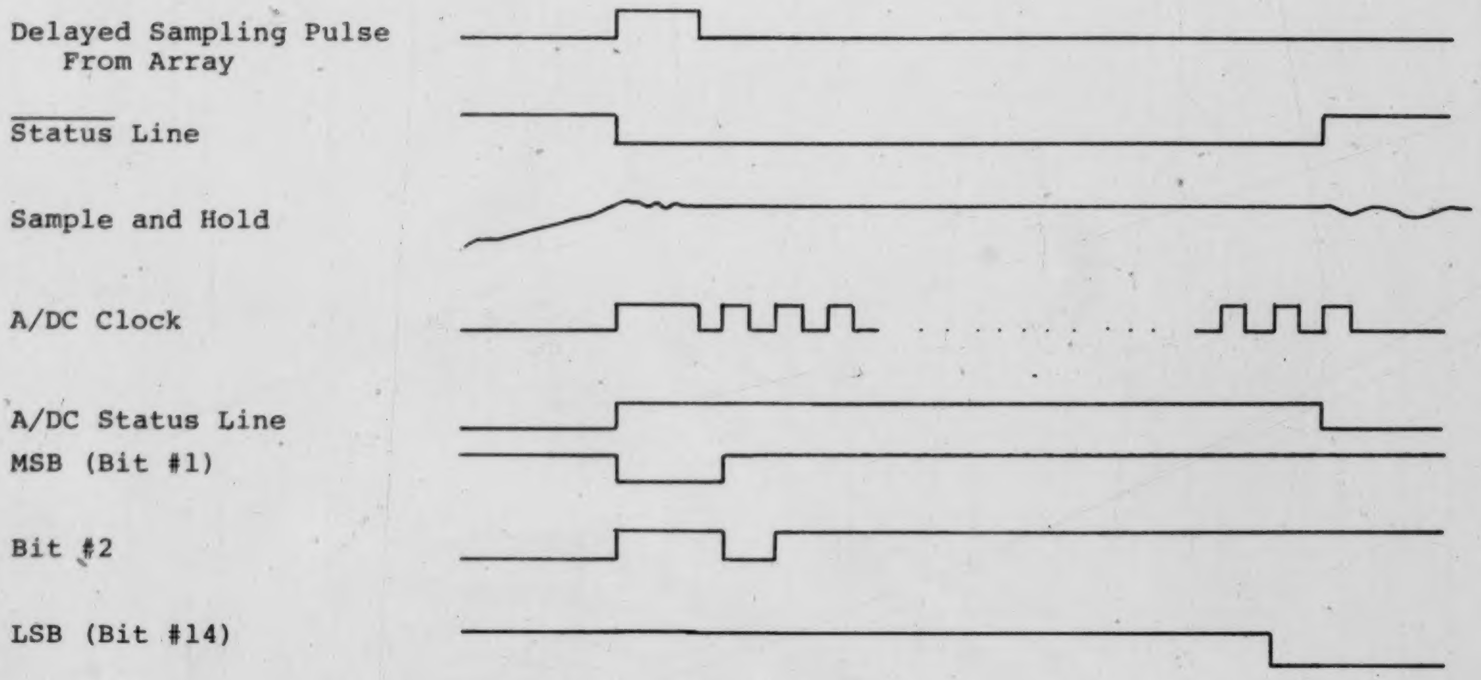

Delayed Sampling Pulse
From Array
$\overline{\text{Status}}$ Line
Sample and Hold
A/DC Clock
A/DC Status Line
MSB (Bit #1)
Bit #2
LSB (Bit #14)

Figure 23. Timing signals for the ADC1131 analog to digital converter.

The data sampling pulse developed from the sample pulses on the array drive board RC1024S is fed to the convert command input of the A/DC. When this signal goes high the $\overline{\text{STATUS}}$ output of the A/DC is forced low to initiate the switching of the sample and hold amplifier from tracking to hold. This requires 50 to 50.5 ns to switch the amplifier and a further 1 μs for the decay of the switching transient. The sampling pulse then goes low and its negative edge initiates the start of the conversion. The sampling pulse must be set to a width of 1.5 μs using the 74121 monostable circuit described earlier (Figure 12) to allow sufficient time for the sample and hold amplifier to settle. During the conversion the A/DC sets the bits in order starting with the most significant. When the least significant bit has been set, the $\overline{\text{STATUS}}$ output of the A/DC goes high, unlocking the sample and hold amplifier which then returns to tracking the analog signal. At the same time the STATUS output of the A/DC goes low and this negative edge is used to trigger the microcomputer so that it records the digital values now latched at the output of the A/DC.

During operation it was found that the sample and hold amplifier over-heated sufficiently to inhibit its function and it had to be fitted with a cooling fan to remove the generated heat.

1.3 The AIM 65 Microcomputer

This is a second generation single board microcomputer based on the 6502 microprocessor. It has several useful input/output (I/O) features which include:

i. A typewriter style alpha-numeric keyboard.

ii. A 20 characters wide electronic alpha-numeric display.

iii. A 20 characters wide thermal printer.

iv. A user I/O connector joined to a 6522 Versatile Interface Adapter (VIA). This has two 8 bit parallel I/O ports and 4 control lines. The user I/O connector also carries interfaces for cassette type tape recorders and a Teletype.

v. A connector designed for further expansion of the computer. It carries the full address, control and data buses from the 6502 microprocessor.

The computer has a monitor in read only memory (ROM) and can be equipped with ROM based assembler and BASIC language interpreters. The computer accepts assembly language mnemonics as well as machine operating codes and this simplifies programming.

A major disadvantage of the AIM 65 as supplied is that it has only 4096 8 bit bytes of random access memory (RAM) available. This has to accommodate the system stack, all of the programming loaded and all of the data collected.

The actual interface connections between the AIM 65 and the A/DC are tabulated in Appendix 3. In summary, the lowest 8 bits of the digitized signal were acquired through the A port of the 6522 VIA and the upper 6 bits through the lower 6 bits of the B port. The STATUS output from the A/DC was connected to control line CA1. The output of the start pulse flip-flop on the RC1024S board (Figure 18) was connected to control line CB1.

2. Programming the Computer

The AIM 65 was programmed to carry out 2 functions. The first was data acquisition for all 128 diodes of a photodiode array. It used signal averaging and had the option of subtraction of a sequentially acquired background signal. The second, calculated signal-to-noise ratios from measurements of the data values for the same photodiode 32 times. It could handle up to 32 diodes at once in a maximum of 4 groups.

Both programs were in 3 parts. The first used BASIC to ask for parameters. The second was in machine language for the acquisition of the data. The last part was in BASIC for calculation and printout of results. The programs are listed in Appendix 4.

The data acquisition rate is governed by the time taken by the AIM to carry out the longest data acquisition and storage loop for each photodiode of the array. In the signal-to-noise ratio program the longest loop took a minimum of 74 cycles of the microprocessor. The AIM runs at 1 MHz so this meant that at least a 74 μs interval was required between successive samplings. In order to leave time for possible changes in programming, the sampling rate was set at 10 kHz to give a 100 μs interval between successive diode readouts.

3. Setting Up the Apparatus

The spectral sources, optical systems and detectors used in our laboratory are designed to be mounted on an instrument rail bed of the type originally developed by Walters [37].

The direct reader was too cumbersome to mount directly on a rail bed but it was mounted on a fixed frame so that the entrance slit matched the height of a spectral source mounted on a rail bed. A short rail bed was placed before the entrance slit and aligned so that a source placed on it would be co-linear with the entrance slit and the centre of the diffraction grating.

4. Finding the Spectral Line

The first positional reference point on the focal plane of the direct reader was made using a helium-neon laser. The laser was set up on the rail bed and the position, with respect to the scale on the exit slit mounting rack, noted for the 632.8 nm wavelength emission.

A No. 4 neutral density filter (1×10^{-4} transmission ratio) was placed before the laser and a photodiode array, mounted on its carriage, set up in the focal plane.

The signal from the RC1024S board, coupled to the array, was fed to an oscilloscope and the integration time set as short as possible. The array carriage was moved and adjusted until the laser signal appeared on the oscilloscope. The carriage was then locked firmly in place on the mounting rail and the laser signal further attenuated by additional filters. The vertical adjustment on the carriage was corrected to give the maximum signal response and the horizontal focussing adjustment corrected to give the highest and narrowest peak. The position of the right side of the array carriage with respect to the scale on the mounting rail was recorded as the primary reference point.

The approximate position of the spectral line sought was calculated from the primary reference point and the reciprocal dispersion of the direct reader obtained from the Jarrell-Ash instruction manual [38]. The array carriage and the RC1024S circuit board together with its auxiliary circuitry were moved to cover the calculated position.

A spectral source was placed on the rail bed and the spectral line located using the oscilloscope. The carriage was then locked in position and adjusted as before. The position of the right hand side was taken as a secondary reference point.

When a hollow cathode lamp was used as a spectral source, it was placed close to the entrance slit to give maximum illumination of the grating. When an inductively coupled plasma (ICP) source was used, it was run as described in Appendix 1. A 1000 ppm solution of the element emitting the sought-after line was aspirated into the nebulizer feeding the plasma.

The first spectral line located with the plasma source was the calcium II line at 393.4 nm. This is a strong emission and was easily found before the illumination of the direct reader by the plasma was optimized. The illumination of the direct reader was then optimized to give a maximum signal value for this first line. (Illumination of the direct reader by a plasma source is discussed in Chapter VII.)

The initial calculation of the line position is important as the array window is only 3.25 mm wide, equivalent to a 1.8 nm spectral window. Consequently spectral emissions are not readily identifiable by their position relative to other spectral features. With experience, some reference to neighbouring spectral lines can be made by careful movement of the array carriage along the focal plane.

Initially the calculation was correct to within 1 cm but as more reference points were established, the array could be placed to within 2 mm.

Line finding was easy over the spectral range of the direct reader down to approximately 270 nm. It was noticeable that the array had to be moved closer to the centre of the Rowland circle, for correct focussing, as the array was moved to the right, towards the lower wavelength region.

At the extreme right of the dark box, line location was more difficult. The focussing adjustment on the carriage had to be moved inwards by more than 1 cm from the setting for the 632.8 nm laser line. There was considerably more depth of focus than at longer wavelengths and the signal could not be brought to such a sharp peak when viewed on the oscilloscope. The responsivity of the photodiodes is lower in this spectral region (Figure 4) than at longer wavelengths. Longer integration times (up to 5 s) were required to find the lines so the results of adjustments were difficult to follow on the oscilloscope. Because the array was tangential to the Rowland circle it was not directly facing the diffraction grating (Figure 2). Consequently it was being illuminated other than normally. As the carriage focus adjustment was made, the spectral line position changed with respect to the array so that the signal as viewed on the oscilloscope moved along the array. In extreme cases, it disappeared out of the array window.

The need for focussing adjustment was caused by inaccuracies either in the placement of the focal plane mounting rail in the direct reader or in the alignment of the diffraction grating. The arc of the mounting rail did not correspond exactly to the Rowland circle of the grating. Fortunately this had been foreseen and the diode array carriage had sufficient adjustment to allow for the correction of the problem.

The single array system was used to determine some of the characteristics of a photodiode array based direct reader. Measurements were made to determine the variability of the detector, its linear range and detection limits for analysis. Several methods were examined for separating the analyte signal from the background.

5. The Variability of the Array Background

One of the limitations of the precision of any analytical determination is the variability inherent in the measuring instrument. For an electronic measurement system background consistency is very important. This was investigated for the single diode array system by observing the diode to diode variation of the signal output in the dark. The dark current itself was reduced by cooling the array to -22°C.

Background values were measured for single runs (no signal averaging) at a series of integration times of from 0.0156 s to 64 s. Thirty six consecutive diodes near the centre of the array were selected and the means and standard deviations calculated separately for the odd and even diodes and for the set as a whole. For this series of measurements the preampifier was set to give an output of 10 V for a saturated array. Some of the values obtained are listed in Table 4 and illustrate several of the problems associated with diode arrays.

Table 4. Background values for 36 diodes at -22°C.

Integration Time Seconds	Mean Values in Volts			Standard Deviation			$F\left(\frac{\text{Even}}{\text{Odd}}\right)$
	Odd Diodes	Even Diodes	All Diodes	Odd Diodes	Even Diodes	All Diodes	
.01563	2.855	2.778	2.817	.01014	.01494	.04132	2.17
.25	2.059	1.984	2.021	.01373	.02675	.04362	3.80
1.0	1.893	1.825	1.859	.01423	.02780	.04071	3.82
4.0	1.321	1.282	1.301	.01411	.02825	.02953	4.01
16.0	.598	.608	.603	.01701	.03454	.02729	4.12
32.0	.905	.931	.918	.02947	.03851	.03634	1.71
64.0	1.479	1.520	1.499	.02351	.03833	.03807	2.66

5.1 Changes in the Background Mean Value

The background mean value changed as the integration time was increased. It decreased with time for about 16 s and then started to increase again. The decrease was due to electronic leakage on the RC1024S board. The later increase was due to the build up of integrated dark current. Because of this background change, the absolute value of a spectral signal, with respect to ground, becomes meaningless. It has to be corrected for background change by reference to measurements made on the same array but away from the spectral signal.

This change in background level with integration time was later investigated for several array temperatures. The results are plotted in Figure 24. The temperature dependence of the integrated dark current is clearly indicated. Other experiments have shown that the linear range of the array remains steady as the background level initially decreases, with integration time, but it diminishes as the integrated dark current builds up. As long integration times are only necessary with low light intensities, an array temperature of -4°C is cold enough to leave sufficient remaining linear range for a spectral measurement at a 64 s integration time.

5.2 Differences Between Odd and Even Diodes

The last column in Table 4 shows the values for F

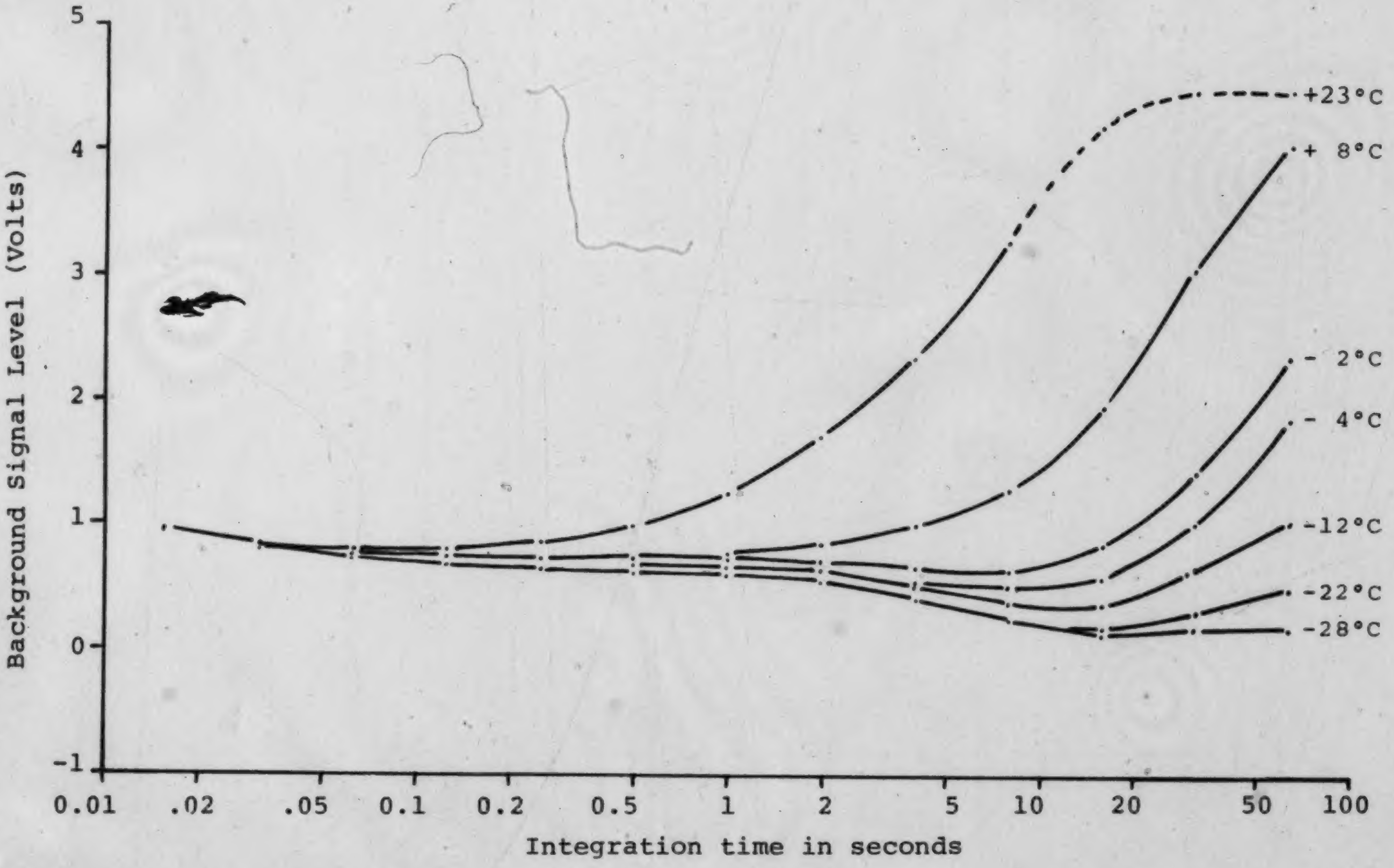


Figure 24. The dependence of background signal level on integration time and array temperature.

(variance ratio) for the even and odd sets of diodes. For the hypothesis that the odd and even diodes form separate data populations, these F values exceed the 99% confidence level for four of the values quoted in the table, exceed the 95% level for two and fail to reach the 95% for the remaining two.

The odd and even diodes are not equivalent in the background. Their readout is controlled by separate shift registers on the array. Their signals come out of the array on separate pins, use separate wires in the ribbon cable, and are processed through separate difference amplifiers, buffer amplifiers and an analog switch before they are combined into a common signal line.

They can be adjusted to the same level in the dark at minimum integration time but their values tend to drift apart.

The mean values given in the table for the odd diodes were greater than those for the even diodes at short integration times but the reverse was true at long integration times. This may have been due to drift, as the experiment took more than half an hour to run, but it was probably due to another variable.

There is a gain-control variable resistance in the feedback loop of the buffer following the difference amplifier in the odd diode processing circuit. As the integration time was increased, the amplifiers had more integrated dark current signal to work on and the gain adjustment may have been set a little low.

The F test showed that the even diodes were more variable than the odd ones. If it were just a question of an offset in their values, their variances would be similar. There is yet another adjustment to be made that would account for this difference in variability. Each shift register in the array is driven by two phase clocks called Ø1 and Ø2 (Figure 5). There are adjustments on the RC1024S board that allow the matching of the outputs of those diodes read out on Ø1 to those read out on Ø2. This adjustment had been more accurately made for the odd diodes than for the even ones. This control does not drift significantly.

The separate variabilities of the odd and even series of diodes do increase with longer integration times and this is likely to cause problems as long integration times will be used with the weaker spectral intensities.

The variations in the background level affect the way the arrays are read out. Because background level drops initially as integration time is increased, the lower end of the range of the analog to digital converter cannot be matched to the background level. Consequently the full 10 V range of the converter cannot be made equivalent to the difference in the saturated and background values for the array output.

For some measurements on the single array system, the range switch on the preamplifier was opened (divide by 3) (Figure 22) and the offset adjusted so that all background and saturation levels fell within the range of the A/DC. This would increase the effect of digitization error if it became significant. A different approach was taken later when the multi-array system was designed (see Chapter V).

The interdiode variation, especially the odd-even variation, is very serious. It can only be adjusted at very short integration times and affects most signal measurements. Later measurements (Chapter VI) were made considering the odd and even diodes as separate populations when background levels were calculated.

6. Noise Measurements

Salin and Horlick [39] have reported on the standard deviation and signal to noise ratio of photodiode array detector systems. They report that, with an ICP plasma source, the signal to noise ratio is independent of the signal strength away from the detection limit. This is because the major noise source is flicker noise in the plasma source and the standard deviation is proportional to the signal strength. They also report that the standard deviation of the array background due to dark current is independent of integration time up to 2.5 s.

The new method for controlling the array allowed measurements to be made with much longer integration times than those used previously. A hollow cathode lamp was used instead of the dark current as a source relatively free from analyte flicker noise. Standard deviations were calculated for background subtracted values by using multiple measurements of the signal for a single diode. Values are given in Table 5 for the diode at the 403.3 nm emission for manganese. The standard deviation remained constant until the integration time was increased to 8-16 seconds and then it started to increase.

The slow increase in standard deviation may be due to low frequency flicker noise as it takes at least 19 minutes to carry out a set of measurements with 16 seconds integration time. There could be slow variation in the output of the hollow cathode lamp spectral source but variability in the measurement system cannot be excluded. For these measurements the preamplifier was set for a gain of 3.3. Consequently, most of the figures in Table 5 represent variations of 1 to 3 millivolts in the outputs from the RC1024S board. This could control the lower detection limit of the diode array if other noise sources were absent. As the upper detection limit is set

Table 5. Standard deviations of a diode output with a constant source.

Integration Time Seconds	Standard Deviation (Millivolts) at			
	-28°C	-12°C	-2°C	+8°C
.0313	-	-	3.2	2.9
.0625	-	2.6	2.9	3.3
.125	3.6	2.6	3.2	2.8
.25	2.6	3.0	2.8	2.4
.5	2.2	2.8	3.0	2.9
1.0	2.6	2.9	2.5	2.6
2.0	3.8	10.9	3.3	2.7
4.0	3.4	2.4	2.5	2.5
8.0	2.6	5.1	2.8	2.7
16.0	7.9	132.	4.7	3.6
32.0	16.0	8.1	9.0	5.5

by saturation at 1 volt, the linear dynamic range of the detector system at a fixed integration time would appear to be between two and three orders of magnitude. The two anomalous results for the -12°C series are difficult to explain. The mean values taken at the same time as these standard deviations corresponded to the expected values for these integration times yet the standard deviation values suggest considerable variation. Simulation calculations have shown that these anomalous results could be achieved by the array failing to respond to one start pulse out of the 32 in the series while the data acquisition system responded to all start pulses. However, no proof of this occurrence can be offered. The -12°C series was the first series run and the effect did not occur in the other 3 series.

7. Proportionality of the Array Signal to Time

A diode array, run at a fixed integration time, has its upper detection limit set by the saturation of the array and its lower detection limit set by the readout noise level. In order to extend the dynamic range, the integration time is changed to bring the output signal within these limits. It is assumed that the array signal will be proportional to the product of the integration time and the light intensity. Horlick and Codding [40] have reported linearity within 1%.

The validity of the assumption was demonstrated by the following experiment.

A hollow cathode lamp intended for steel analysis by atomic absorption was used as a steady light source. The array, cooled to -22°C, was set up to detect the manganese triplet at 403.1, 403.3 and 403.4 nm. The preamplifier was set to give an array saturation value of approximately 10 volts at the A/DC. The entrance refractor plate of the direct reader was adjusted to get a maximum signal value for the centre peak (403.3 nm), by moving the centre of the peak to correspond to the centre of a photodiode. Measurements were made over a range of integration times of from 0.0156 s to 64 s by averaging 10 scans with 10 scans of dark current subtracted. The results are graphed in Figure 25. The array signal was proportional to time over more than two orders of magnitude, and for the centred 403.307 nm peak to three. Fortunately, the signal output from the hollow cathode lamp was strong enough to demonstrate, within the available integration times, both the upper limit of linearity due to saturation and the lower limit shown by the deviation of the weakest peak (403.45 nm) as its measured signal approached the noise level of the array. The linear range of the array corresponds to that suggested in the section on noise measurements.

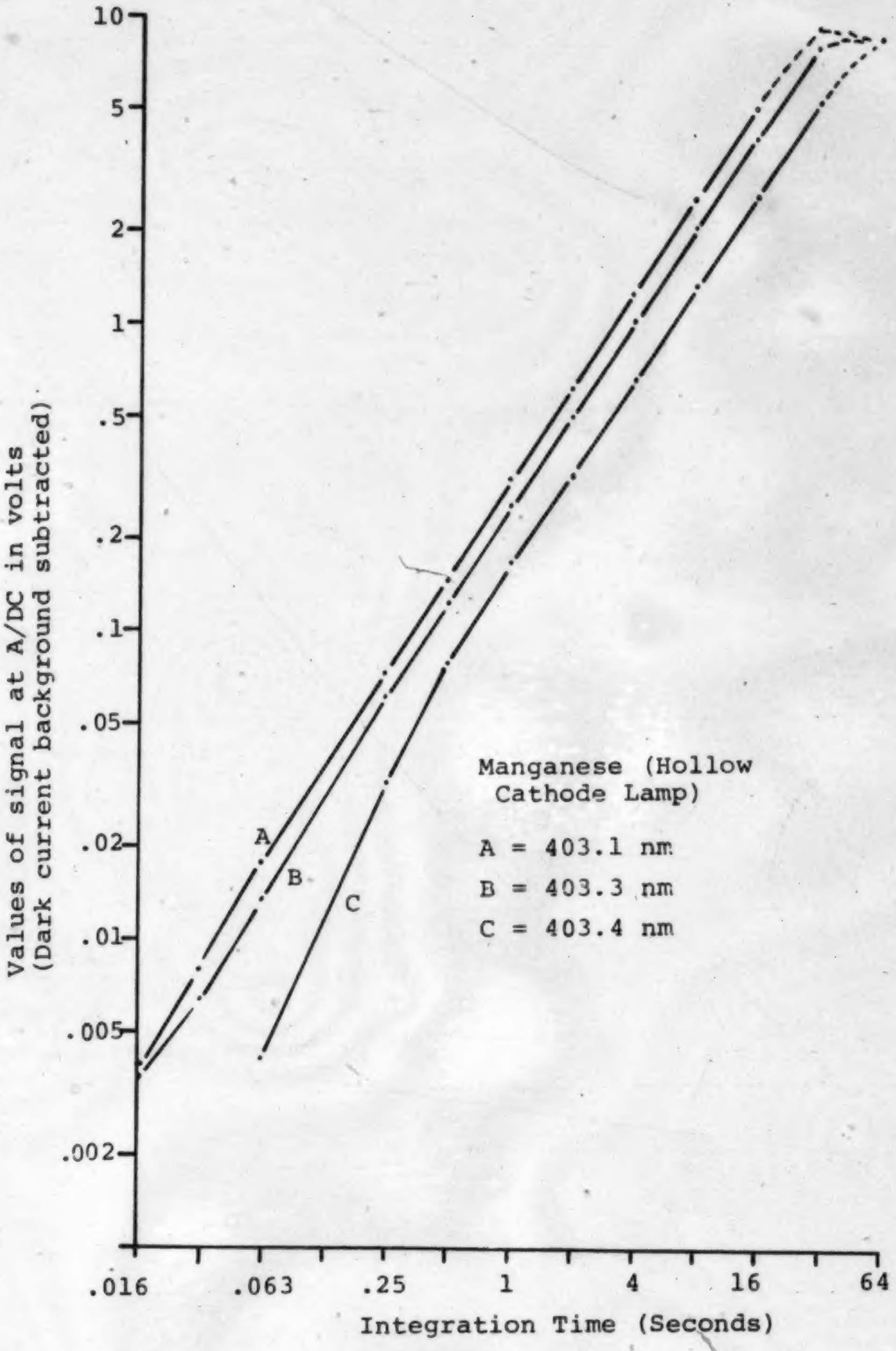


Figure 25. The proportionality of the array signal to integration time.

The validity of the proportionality assumption allows the light intensity falling on a photodiode to be represented by the value of the output signal (after suitable background corrections) divided by the integration time. This gives a measure of the total light intensity affecting a single diode normalized to a 1 s integration time.

The linear detection range of the photodiode array direct reader should then be obtained from the product of the linear range of the array and the available range of integration times.

8. Spectral Measurements Using an ICP Source

The performance of an analytical instrument can only be tested properly by using it for analysis. The single array system was used for independent measurements of 6 elements. Information was obtained on the linearity of the system, detection limits and on the use of simple methods of background correction.

Separate solutions were prepared for cadmium, calcium, magnesium, manganese, strontium and zinc, all at 1000 ppm concentration. These were diluted in tenfold steps to give a series of solution concentrations extending down to the expected detection limit for each element. Double distilled and deionized water was used for all dilutions. The solutions were aspirated into the spray chamber of an inductively coupled plasma source. (Operating conditions of the ICP are given in Appendix 1.) The spectral emissions of the 6 elements chosen fall in the wavelength range of 238 to 408 nm.

The preamplifier to the analog to digital converter was set in the low gain position to allow the use of the whole range of integration times from 0.0156 s to 64 s. All data were the signal averaged values for 5 consecutive diode array integrations. Where the background was corrected by subtracting the signals generated by aspiration of water, this was done immediately by the use of the subtraction loop in the data acquisition program (Appendix 4).

8.1 Measurements with Calcium as Analyte

The calcium II line at 393.4 nm is a very intense emission in the ICP and was chosen to illustrate the linear range of the detection system that could be obtained by varying the integration time. The system responses are shown in Table 6. The parameter recorded is the peak height voltage, at the A/DC, normalized to a 1 second illumination by dividing by the integration time.

The first set of values (A) are the water background subtracted values. The second set (B) is similar to set (A) but has been further corrected using a factor obtained

Table 6. Photodiode response to calcium 393.4 nm. Values are in volts at the A/DC normalized to a 1 second integration time.

PPM (PPB)	A Water Signal Subtracted	B A + Correction	C Corrected only
1,000	87.4	86.5	79.9
100	14.5	14.4	--
10	1.58	1.57	1.59
1	.152	.149	.149
(100)	.0139	.0138	.0136
(10)	.00153	.00155	.00153
(1)	.000254	.00020	.00013

from the values for off-peak diodes close to the response peak. The third set (C) are values without the water background subtraction but using the correction factor obtained from off-peak diodes. The use of water background subtracted values required about 12 minutes to run at 64 s integration time with the possibility of low frequency flicker noise affecting the subtraction. The off-peak correction factors for calcium were calculated from groups of 7 and 8 consecutive diodes starting 7 diodes away from the peak. They helped to compensate for any flicker noise in the system other than that due to the analyte.

The results listed in Table 6 indicate that the use of the off-peak diode generated correction factor gives linearity as good as that obtained using the water background subtraction method. This is subject to certain reservations. The array must be free from defects (glitches) in the peak region and in the background evaluation region. The peak must not be subject to interference from wavelength dependent spectral features such as argon lines and OH molecular spectra unless they can be corrected for. The response of the individual diodes to light must not vary significantly. Hog [41] reported that for an earlier type of diode array, the RMS value of the interdiode variability was about 0.1% and that the end-to-end variation over 256 diodes was of the order of 2%.

The variation in the integrated dark current among the group of diodes must be insignificant. This is not true at room temperature as observed by Vogt [25] and others, including this current work. It can be calculated that the thermal generation of hole-electron pairs and hence the integrated dark current is reduced by a factor of 71 by cooling the array from +23°C to -20°C. As a good quality array, running with a gated oscillator, takes about 16 seconds to saturate with dark current at 23°C, an array at -20°C and integrated for 64 seconds has 6% of its dynamic range taken up by dark current. Dark current measurements would have to be made for each individual array to determine the variability as there is considerable variation of this property between arrays.

The odd-even diode difference must also be considered when calculating the off-peak correction factor. If this difference is large, the odd and even diodes can be considered to form 2 separate populations. In that case the off-peak background correction factor must be calculated from diodes of the same odd-even parity as the analyte peak diode.

The concept of using an off-peak correction factor is not new. It was used by Vogt [25] to save time when using a liquid nitrogen cooled array with integration times of over one hour to study star spectra.

The value given in Table 6 for the water background subtracted signal for 1 ppm calcium solution was actually a mean value for 6 determinations at different integration times. The individual parameter values are shown in Table 7.

The values in Table 7 were calculated from voltages at the A/DC ranging from 20 millivolts to 4.423 volts depending on integration time. When this is considered, the values are remarkably close. Digitizing error is not involved. The value of the least significant bit of a 14 bit A/DC operating over a 10 V range is 0.6 mV. This would cause, at the most, a 3% error in a 20 mV signal. The odd-even pattern contribution was calculated separately and found to be insignificant. Some of the variation with integration time may be due to the multiplication of noise at low signal levels and short integration times. This should not be a serious problem as in analysis low signal levels will be associated with long integration times.

The use of longer integration times to improve detection limits is illustrated in Table 8.

The values are for a relatively low concentration. They were water background subtracted and were calculated

Table 7. 1 ppm calcium measured with various integration times. Values are volts normalized to 1 second integration time.

Seconds Integration	A Water Subtracted	B A + Correction
32.0	.1382	.1378
16.0	.1490	.1487
8.0	.1499	.1483
2.0	.1551	.1553
.5	.1543	.1519
.125	.1624	.1529
Mean	.1515	.1492
Standard Deviation	.0081	.0062

Table 8. Signal to noise ratios with a low analyte concentration (Ca 10 ppb).

	Integration Times		
	16 s	32 s	64 s
Signal to Noise Ratio	5.6	10.7	24.1
Mean Volts	.0221	.0574	.0892
Standard Deviation	.0040	.0054	.0037
Mean / Int. Time	.0014	.0018	.0014

from 32 successive signal values for the same diode (and 32 water background values subtracted).

Close to the detection limit the limiting noise level is due to the measurement system which is independent of the analyte concentration and the integration time (if the array is cold enough). The analyte signal is proportional to integration time so, as the latter is increased, the signal to noise ratio is increased. If the detection limit is taken as the concentration at which the signal to noise level is 3, then the table values indicate a detection limit of 5.4 ppb decreasing to 1.25 ppb as the integration time is quadrupled from 16 to 64 s. The ultimate low level of the detection limit would appear to be governed by the limit of the integration timer circuit, the electronic stability of the system and the operating temperature of the array.

A logarithmic plot of the diode array response to the CaII line at 393.4 nm is shown in Figure 26. For this strong emission, it is possible to cover more than 5 orders of magnitude of concentration values by combining control of integration times with the dynamic range of the photodiode array.

The curvature of the line at high concentrations may have been partially due to self absorption but it certainly was partially due to error in the calculation of

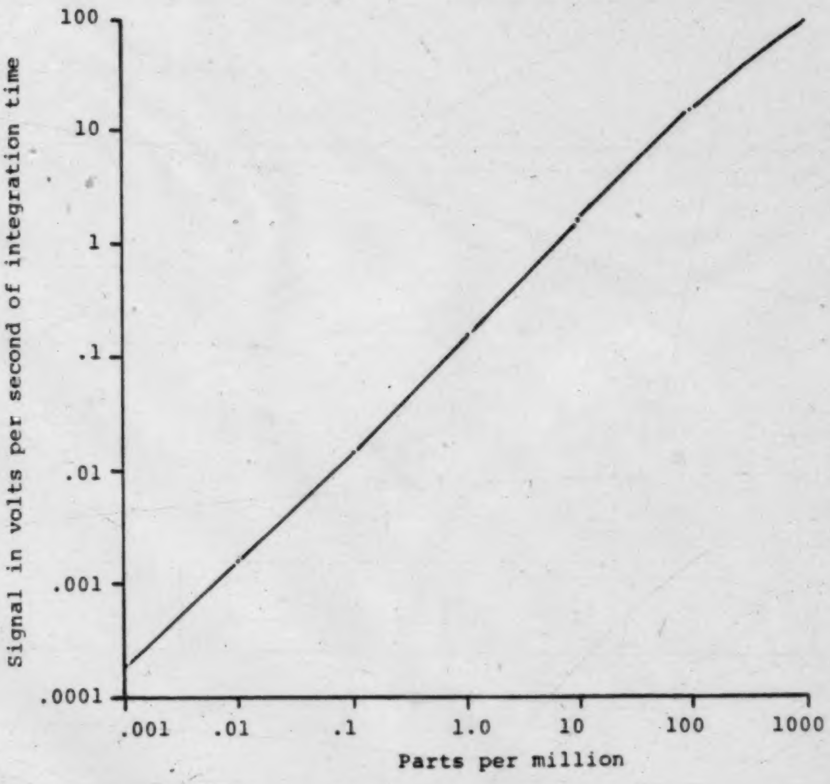


Figure 26.

The diode array response to calcium concentration for the CaII 393.4 nm emission.

the base line value from off-peak diodes. This was caused by collision broadening of the spectral line within the plasma source. This effect is increased for some emissions as the linear Stark effect occurs due to interaction with the plasma electrons [12]. This line was sufficiently broad for the 1000 ppm concentration that its wings overlapped onto the diodes used to calculate the off-peak correction factor. It can be seen from Figure 27 for the signal from 1 ppb concentration that the broadening effect persists down to very low calcium concentrations. In summary, the calcium experiments have shown:-

i. The measurement system has good linear dynamic range for a strongly emitted spectral line.

ii. In favourable circumstances, the base line used for measurements can be obtained from the same array measurements as the analyte signal.

iii. Detection limits are improved in proportion to increases in integration time.

iv. The noise level near the detection limit is again due to the detection system.

8.2 Measurements with Magnesium as Analyte

Magnesium has its two strongest plasma emission lines close enough together for a single array to record both of them. At 280 nm they are of shorter wavelength than the calcium line already discussed.

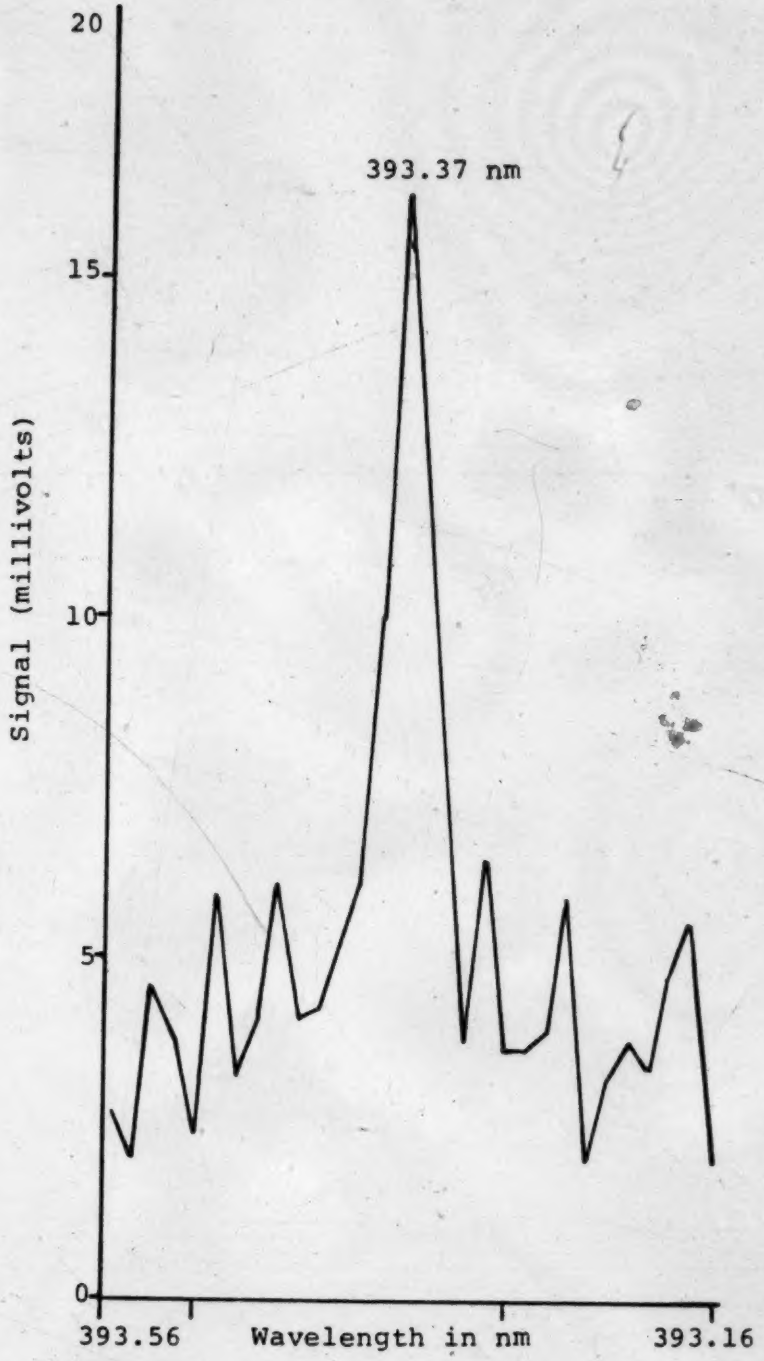


Figure 27. The Ca II peak at 393.4 nm for 1 ppb calcium.

The water subtracted values are given in Table 9. All of the values in the table are water background subtracted data, with and without the use of off-peak diode correction. The two peaks were 53 diodes apart on the array and the off-peak correction factor (background level) was taken from 15 diodes in the centre of the gap between them. Values are also shown for attempts to measure peak area by summing values for the peak diode with those for 5 diodes on either side. The off-peak correction factor was then applied 11 times. The peak area concept was considered in case it had to be used to correct for geometric changes in the position of the diode array. The values for the 2 spectral lines correspond to each other for concentrations of 100 ppm and less. The peak area calculations correspond to approximately three times the value of the central diode signal except at the lowest concentration levels, where they lose precision.

Kubota [42], using a microchannel-plate, image intensified, diode array, has used signal to noise ratios to show that the use of peak area is less precise than peak height. He explained it as due to the increased significance of detector dark current variation and source background variation at the wings of the peak.

Figure 28 is the logarithmic plot of the array response to the two lines.

Table 9. Photodiode response to magnesium. Values are volts at the A/DC normalized to 1 s integration time.

	Water Subtracted 280.3 nm		Water Subtracted 279.6 nm		
PPM (PPB)	Not Corrected	Corrected	Not Corrected	Corrected	11 Diode Sum
1,000	15.43	15.19	20.65	20.44	63.4
100	1.910	1.921	3.50	3.49	10.5
10	.2140	.2130	.430	.429	1.17
1	.0215	.0215	.0440	.0439	.127
(100)	.00191	.00190	.00411	.00409	.0118
(10)	.000176	.000166	.000334	.000323	.00078

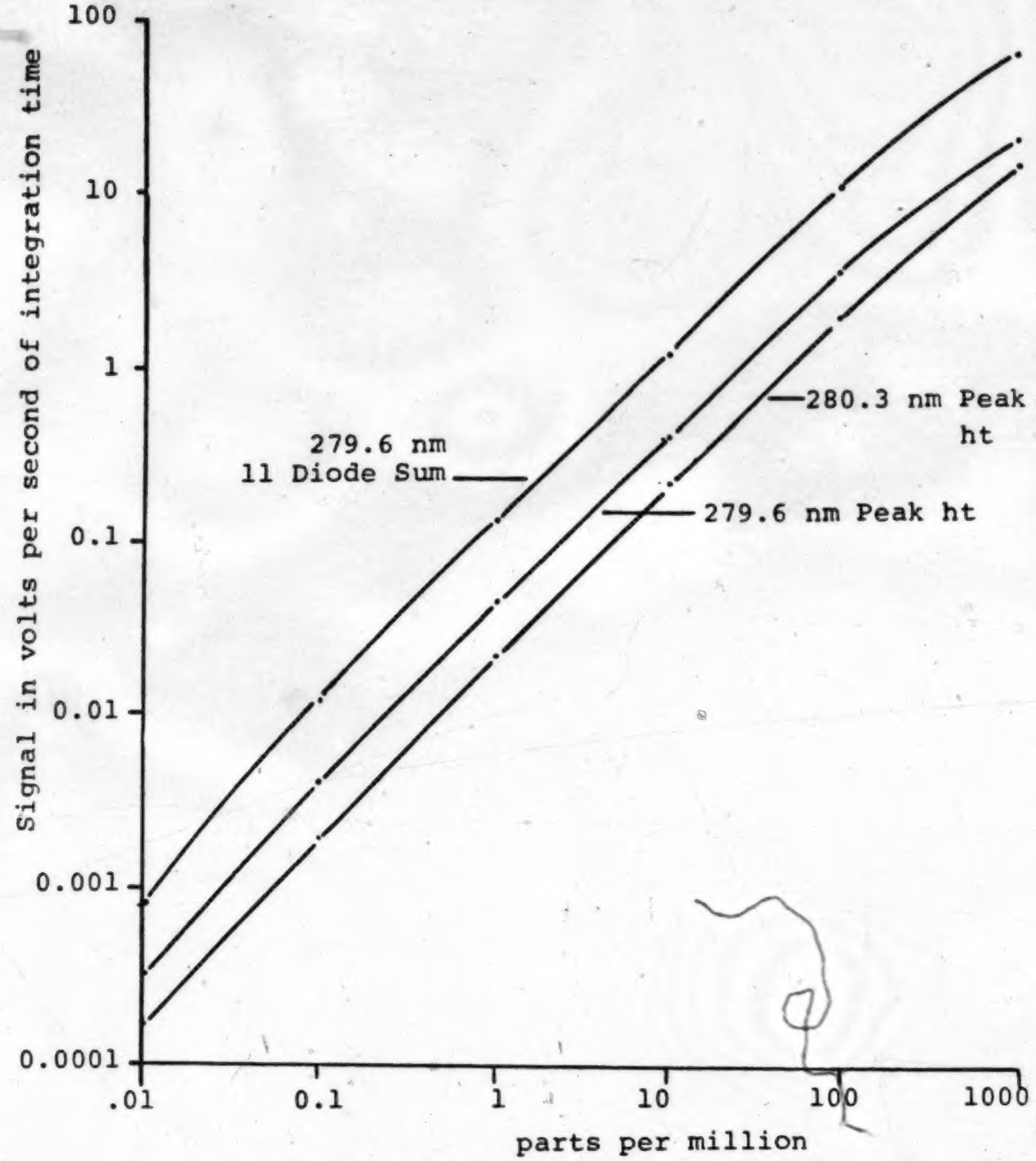


Figure 28. The diode array response to magnesium concentration for the MgII emissions at 279.6 nm and 280.3 nm.

A signal to noise measurement was made for the 10 ppb concentration based on the method of repetitive measurements of the peak value and water background subtraction. The value obtained for the signal to noise ratio was below 1, suggesting that the solution concentration was well below the detection limit. The signal averaged values for 5 runs shown in Figure 29 show that the peaks are still well above the detector noise level as obtained from values of successive diodes in the background.

The repetitive determinations method for signal to noise ratio takes 70 minutes to run with 64 s integration times and is sensitive to low frequency variation such as a DC level drift. If the analyte peak is measured with respect to the variation among the diodes of the same measurement it can still be evaluated regardless of DC level drift.

In summary the magnesium experiment has shown:-

i. The responses to two spectral lines maintain a close ratio over several orders of magnitude.

ii. Peak heights have better precision than peak areas at low analyte concentrations.

iii. Signal to noise ratios obtained from repetitive measurements of a single diode output can give a false indication of the detection limit.

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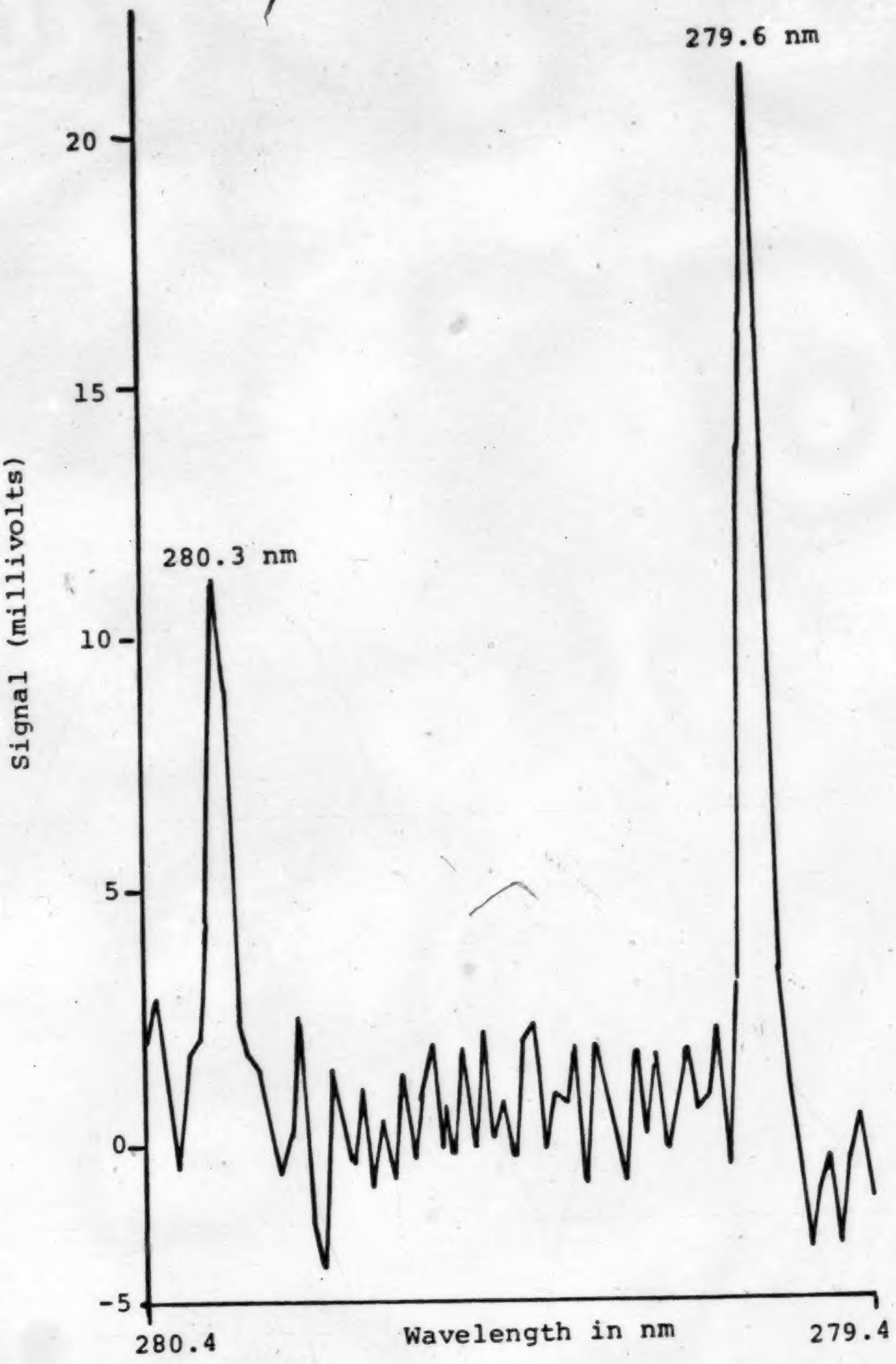


Figure 29. The magnesium peaks at 279.6 nm and 280.3 nm for 10 ppb magnesium.

8.3 Measurements with Cadmium and Zinc as Analytes

These elements were chosen because the spectral lines used for their analysis are much lower in wavelength than those of the other elements chosen. The cadmium II 226.5 nm and zinc I 213.86 nm emissions were very difficult to locate as they were low in intensity and required considerable focussing adjustment of the array carriage. The diode array responses are given in Tables 10 and 11. The response curve for both cadmium and zinc is shown by Figure 30. The zinc peak at 1 ppm concentration is shown by Figure 31.

The array responses to these elements was expected to be lower than for calcium but the values obtained were much lower than expected.

8.4 Measurements with Manganese as Analyte

The manganese lines chosen were the manganese I triplet at 403.08 nm, 403.31 nm and 403.45 nm. These same lines had been previously used with the hollow cathode lamp source to establish the linearity of the array. They are close enough together to be recorded simultaneously and illustrate the resolution capable with the diode array detector. The array responses are given in Table 12. All values were water background subtracted and adjusted with the off-peak correction factors. The response curves are given in Figure 32. Measurements across the three peaks,

Table 10. Photodiode response to cadmium. Values are volts at the A/DC normalized to 1 second integration time.

PPM	Water Subtracted	Corrected Water Subtracted	Corrected Only	11 Diode Sum
1,000	.241	.238	.244	.769
100	.0278	.0276	.0258	.0906
10	.0031	.0031	.0031	.0102
1	.00039	.00033	.00032	.00103

Table 11. Photodiode response to zinc. Values are volts normalized to 1 second integration time.

PPM	Water Subtracted	Corrected Water Subtracted	Corrected Only	11 Diode Sum
1,000	.403	.401	.421	1.39
100	.0436	.0447	.0449	.146
10	.00537	.00535	.00538	.0165
1	.00049	.00045	.00044	.00212

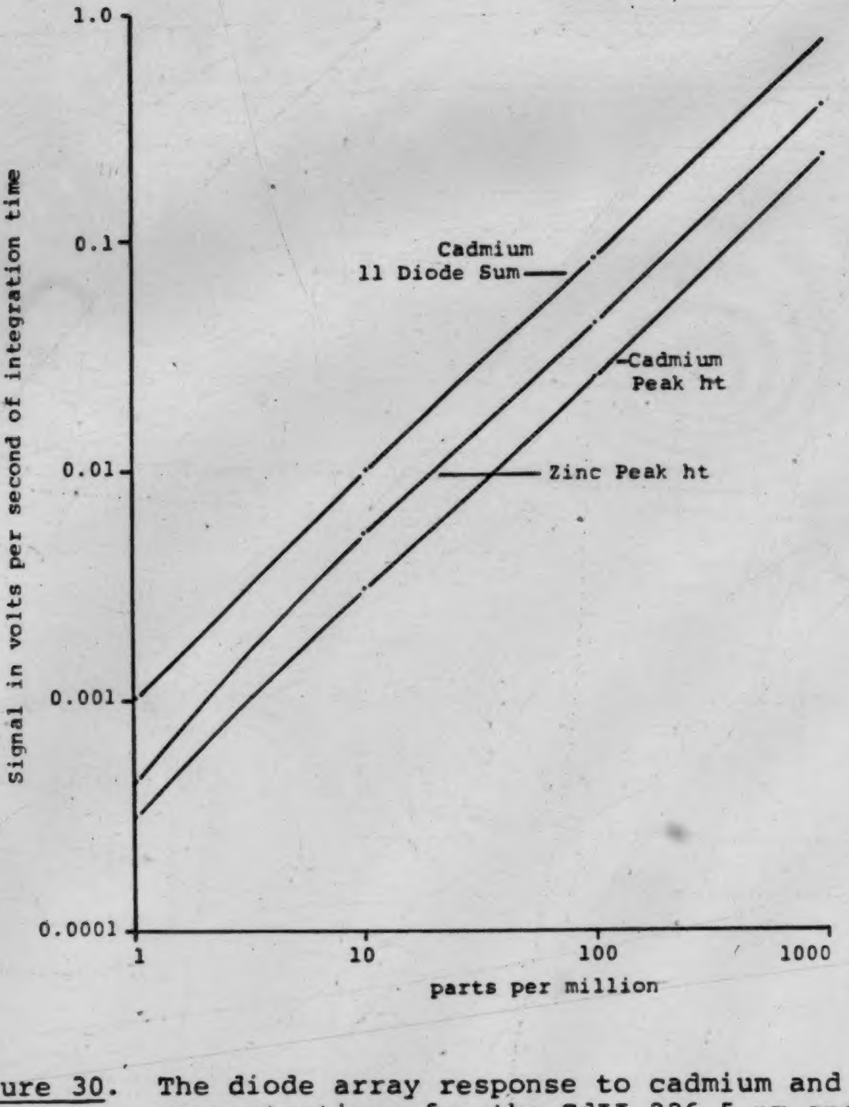


Figure 30. The diode array response to cadmium and zinc concentrations for the CdII 226.5 nm and ZnI 213.9 nm lines.

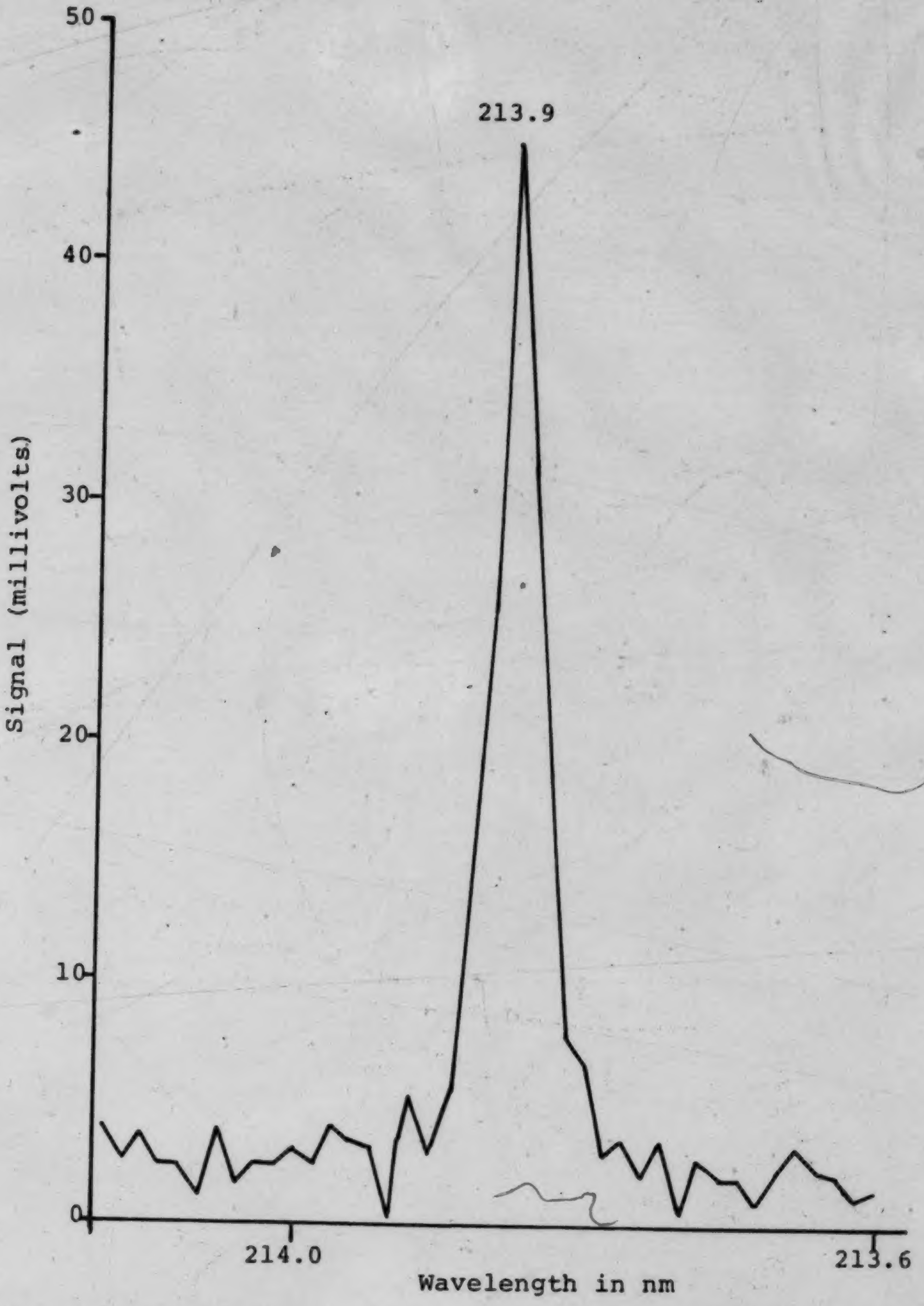


Figure 31. The zinc peak at 213.9 nm for 1 ppm zinc.

Table 12. Photodiode response to manganese. Values are volts at the A/DC normalized to 1 second integration time.

PPM (PPB)	403.45 nm	403.31 nm	403.08 nm	
			Peak Height	11 Diode Sum
1,000	.875	1.39	1.76	3.27
100	.070	.126	.154	.325
10	.0075	.0132	.0184	.0330
1	.00067	.00109	.00177	.00313
(100)	.000054	.00019	.00017	.00037

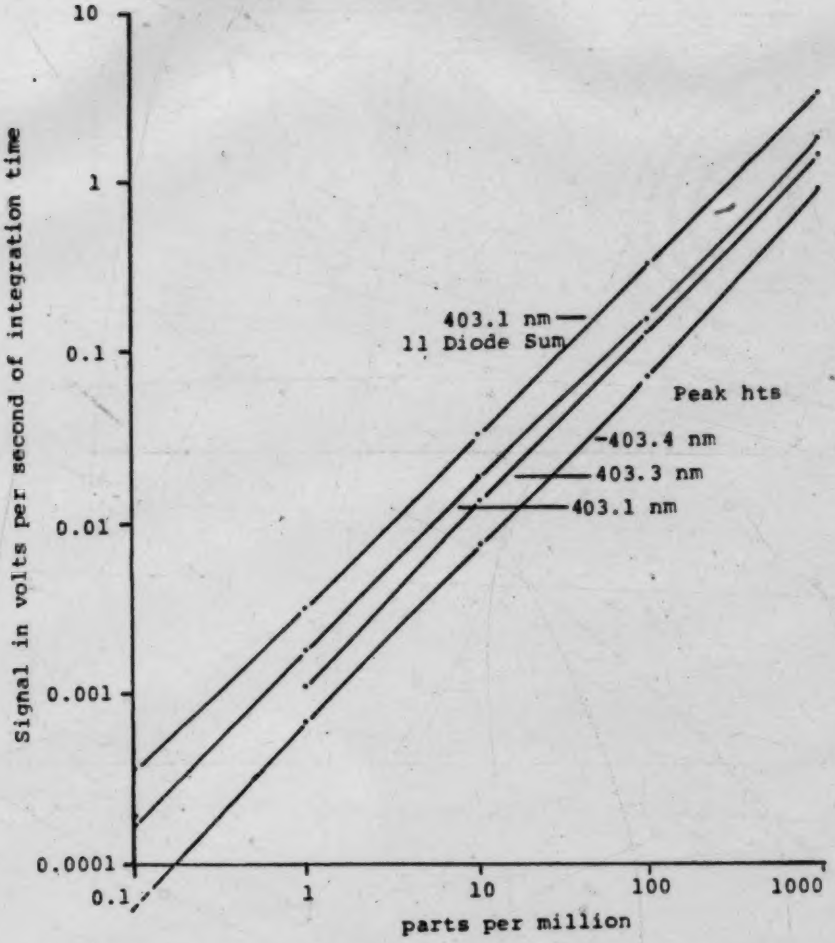


Figure 32. The diode array response to manganese concentration for the MnI triplet at 403.1 nm, 403.3 nm and 403.4 nm.

showing the resolution, are illustrated by Figure 33 for the 1 ppm concentration of manganese. The 11 diode sum values (peak area) were twice the value of the peak height, compared to triple the peak height for magnesium, cadmium and zinc. The manganese lines appear to be narrower than those of the other elements. This is probably due to the position of the manganese lines which are formed close to the normal of the centre of the grating. Here astigmatism is less than at the lower wavelength positions on the focal plane.

In summary, the manganese experiment has shown:-

i. An example of base line resolution for two spectral lines separated by only 0.14 nm.

ii. An example of a much narrower spectral line than those obtained with the other elements examined.

8.5 Measurements with Strontium as Analyte

Strontium was chosen as it emits about 100 times as intensely as the manganese lines in the same spectral region. Like the calcium II line at 393.4 nm, strontium II 407.8 nm is affected by the linear Stark effect and should have a completely different profile than the manganese lines. The experimental values are given in Table 13.

The loss of linearity at the high concentration is mainly due to self absorption in the source as the off-

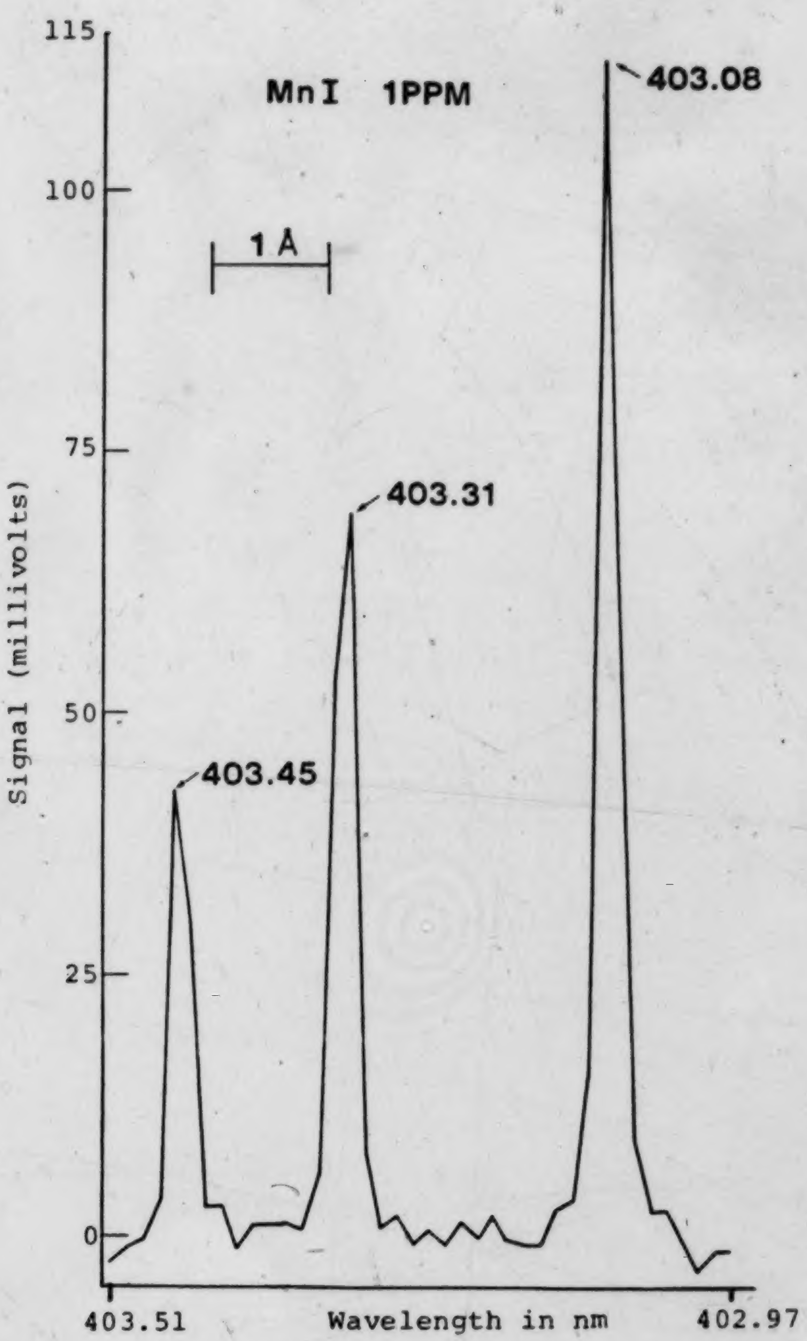


Figure 33. The manganese 403 nm triplet at 1 ppm manganese.

Table 13. Photodiode response to strontium. Values are volts at the A/DC normalized to 1 second integration time.

PPM (PPB)	Water Subtracted	Corrected Water Subtracted	Corrected Only	11 Diode Sum
1,000	74.5	74.2	75.5	224.5
100	15.0	15.0	14.8	43.1
10	1.80	1.79	1.79	5.02
1	.179	.179	.181	.50
(100)	.020	.020	--	.062
(10)	.00165	.00174	.0021	.0054

peak correction factor was calculated from diodes well away from the peak. The eleven diode sum values were approximately three times the peak height. The peak for the 10 ppb concentration is shown as the solid line in Figure 34. The dotted line is for the 403.8 nm line of 1 ppm concentration of manganese, drawn to the same scale and is included to give an indication of the degree of broadening of the strontium line.

8.6 Discussion of the Detection Limits Found

The photodiode array responses for spectral lines in the centre of the direct reader were excellent but those for cadmium and zinc were very poor. A table of detection limits of 70 elements for analysis by the inductively coupled plasma has been published by Winge, Peterson and Fassel [43]. The diode array was able to detect elemental concentrations close to those published for spectral lines in the centre of the direct reader focal plane, but not for those to the right side, in the ultra-violet.

Calculations have been made to determine the concentration limits for the diode array direct reader by a similar method to that used for the published results. Response signals were taken for solution concentrations sufficiently high above the detection limit that confidence in the values obtained was high. The concentrations chosen were still low enough for the

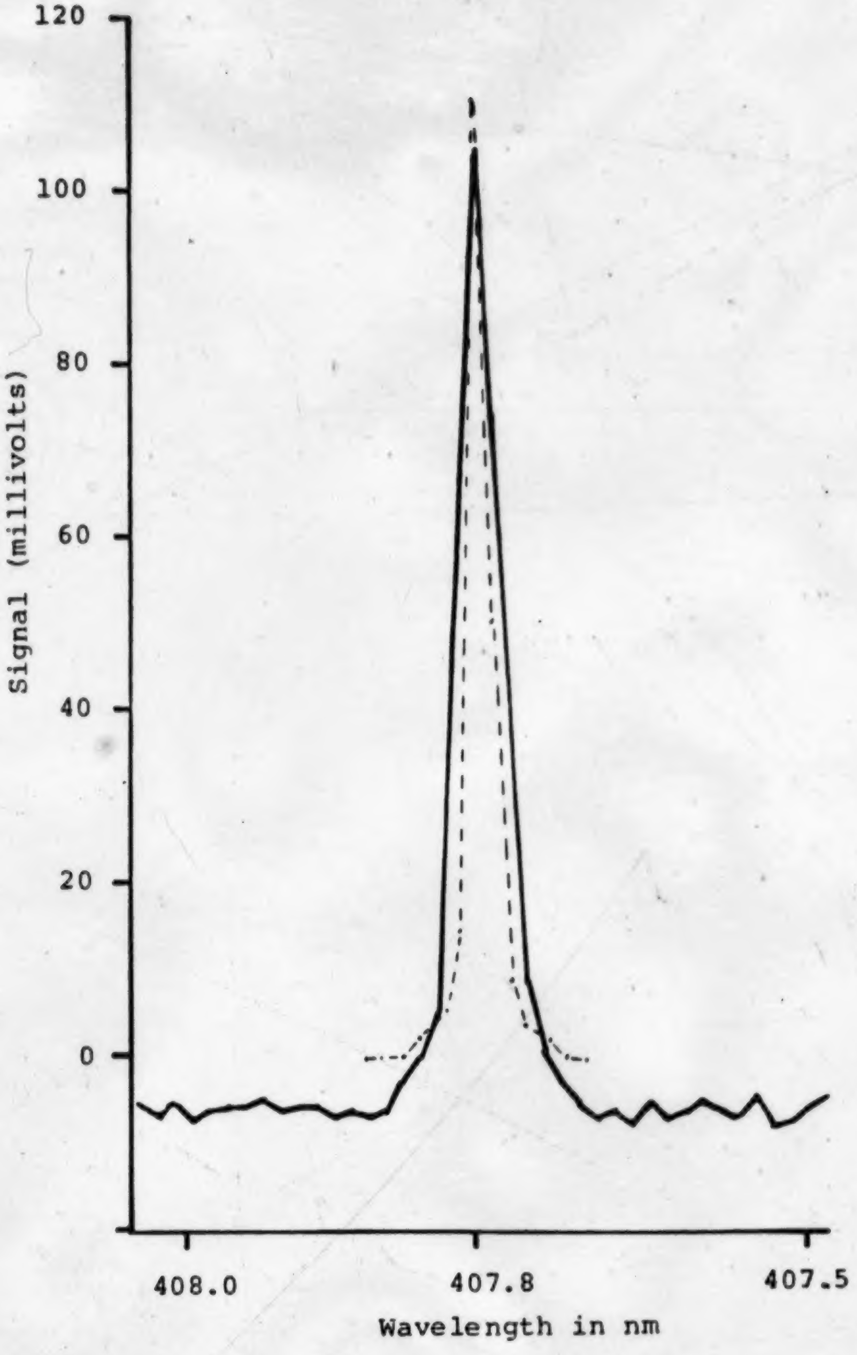


Figure 34. The strontium 407.8 nm line at 10 ppb strontium. The dashed line is the 403.8 nm line for 1 ppm Mn drawn to the same scale to show the Sr line broadening.

limiting noise to be due to the measurement system so that the same noise level could be applied at the detection limits. The noise values (standard deviations) were calculated from the values of off-peak diodes. The detection limit was calculated as that concentration at which the signal level would equal three standard deviations of the background signal. The detection limit values are calculated and compared to the published values in Table 14. (The standard deviation for calcium was high as the off-peak diode values used to calculate the noise level were still on the wings of the broadened line. Consequently the noise would contain some contribution due to the calcium concentration.)

As low values for detection limits are desirable, values in the last column of the table of greater than one favour the diode array system. Values of below one do not.

The comparison values are obviously wavelength dependent as they change by 2 orders of magnitude as the wavelength decreases from 407.8 nm to 213.8 nm. This indicates an instrumental effect. Talmi and Simpson [23] have published a quantum efficiency curve that indicated that the photodiode quantum efficiency at 210 nm is 75% of that at 400 nm. Salin and Horlick [39] reported that the detection limit for zinc was 50 times that of calcium when

Table 14. Comparison of detection limits with published values.

	Diode Array Values					Det. Limit Ref [43] PPM	Ratio $\left(\frac{\text{Ref [43]}}{\text{Diode Values}}\right)$
Element Line	Test Conc.	Peak Height (V)	Std. Dev. (V)	S/N Ratio	Calc. Det. Limit PPM		
Sr 407.8 nm	.1 ppm	1.281	.0011	1,165	.00026	.00042	1.6
Mn 403.3 nm	1 ppm	.070	.0012	58.3	.051	.047	.92
Mn 403.1 nm	1 ppm	.113	.0012	94.2	.032	.044	1.4
Ca 393.4 nm	.1 ppm	.882	.0020	441	.00068	.00019	.28
Mg 280.3 nm	.1 ppm	.121	.0015	80.7	.0037	.00030	.081
Mg 279.6 nm	.1 ppm	.262	.0015	175	.0017	.00015	.088
Cd 226.5 nm	10 ppm	.199	.0010	199	.15	.0034	.023
Zn 213.8 nm	10 ppm	.343	.0012	286	.11	.0018	.017

using a diode array with a monochromator. The diode array direct reader gave a ratio of 154 to 1. Consequently the use of a photodiode detector to replace a photomultiplier tube was not responsible for the signal loss. The real reason for the loss in response at low wavelengths lies in the age of the instrument.

The diffraction grating of the diode array direct reader was blazed for 360 nm [44]. The luminosity of a blazed grating falls off rapidly on the short wavelength side of the blaze [45] so the diode array cannot respond to light that it doesn't receive. The grating was blazed for this wavelength because it was supplied with DC arc and AC spark spectral sources. These used classical spectral lines that were originally established for their photographic response and were generally of longer wavelength than most useful lines from the ICP. This instrument was designed at least 3 years before the introductory papers on the plasma source were published by Greenfield [46] and Fassel [47].

By contrast, Winge's instrument [43] was designed for the ICP source with a diffraction grating blazed for 250 nm emission. This blaze is now used because the most prominent lines for 45% of the elements usually analyzed with the plasma source are in the 200 to 250 nm region [43].

Consequently, the low response obtained for the diode array in the ultraviolet region must be considered as an instrumental problem due to the grating. It should not be considered as a barrier to its acceptance as a direct reader detector. Later work has confirmed that the limitation is due to the grating by showing stronger signals for cadmium and zinc measured in second order when compared to those measured simultaneously in first order (Chapter VII).

CHAPTER V

A MULTI ARRAY SYSTEM

The experiments with the single array system have shown that the photodiode array can be operated to give similar detection limits for emission spectroscopy as the photomultiplier tube. A direct reader has to have several spectral windows in order to measure the emission from several elements simultaneously. This requires a more complex control and data logging system than was used for the single array system.

Six 128 diode arrays were available and a system was required that would run all 6 under computer control for readout and data storage. Additionally, every array had to be supplied with power, a cooling system and control signals. All of the supply lines had to be flexible to allow the array to be moved around the direct reader focal plane to suit the analytical task.

1. The Data Logging Method

A commercial, photomultiplier tube based direct reader has one channel and detector tube per element. It simultaneously records the time integrated values for the anode current for each tube in analog form. Then it sequentially processes the stored data, element by element. Because the light detector and the signal storage device are separate parts of the circuit, both can have a large dynamic range. This, in turn, allows the signals on all channels to be integrated for the same length of time.

A diode array works differently. The individual diodes are both detector and signal storage devices. In order to obtain a large dynamic range, the integration time must be varied. When the integration time has elapsed, the data processing system must accept the analog signals from the diode array circuit board, digitize them, and store them, all in real time.

A data logging system can only handle one signal at a time so to have several arrays completing their integration times simultaneously and competing for a single analog to digital converter would be a calamity.

One approach would be to have an independent data acquisition system for each array and a master computer to control them all. For six arrays, this would require not only seven microcomputers but in addition, six high speed analog to digital converters, each with its own sample and hold amplifier, and probably cooling fan, and sufficient direct current power supply at several voltages to drive them all.

The alternative approach that was chosen used a single microcomputer and avoids readout clashes by careful control of the integration times. This was done by allowing the integration times to be increased in a stepwise fashion with sufficient time allowed in each step for readout of all six photodiode arrays.

2. The Apple II+ Computer

The AIM 65 microcomputer, although it adequately processed the data from a single photodiode array, was not suitable for the more complex task of handling six arrays. Its limited amount of random access memory (RAM) could have been extended but its slow rate of communication with off-line systems could not easily be improved. Sequential searching of cassette tapes for programs and data is a very slow process. Interfacing with the operator had to be done through the small onboard printer as the single line electronic display could only carry a limited amount of information at any one time. Additionally, the AIM is an engineer's development machine and the little supporting peripheral hardware that is available has a limited market and is consequently expensive.

The Apple II+ is a general purpose microcomputer that uses the same type of microprocessor (6502) as the AIM but it is better designed for rapid and easy interfacing with both the operator and peripheral devices.

The main circuit board of the Apple does not have any built in input/output (I/O) devices. However, it does have the necessary interfaces for easily fitting such devices. The interfaces are shown in Figure 35.

The power, speaker and keyboard connectors are used internally by the computer. The video output connector is a standard RCA phono jack that is usually connected to a video monitor. The game I/O connector is a standard 16 pin DIP socket. It is designed to interface with hand held control devices for playing video games but it is very useful in more scientific applications. It can be used to input and output control pulses, output steady state logic levels and act as a controllable short interval timer, all under software control.

The eight peripheral slot connectors (0 to 7) simplify input and output for the Apple. Each one is connected to the computer's data, address and control buses, the power supply and the system drive clock. In addition, the address bus on the main board is partially encoded to give three low level pulses that are used to select the slot connectors and hence their attached

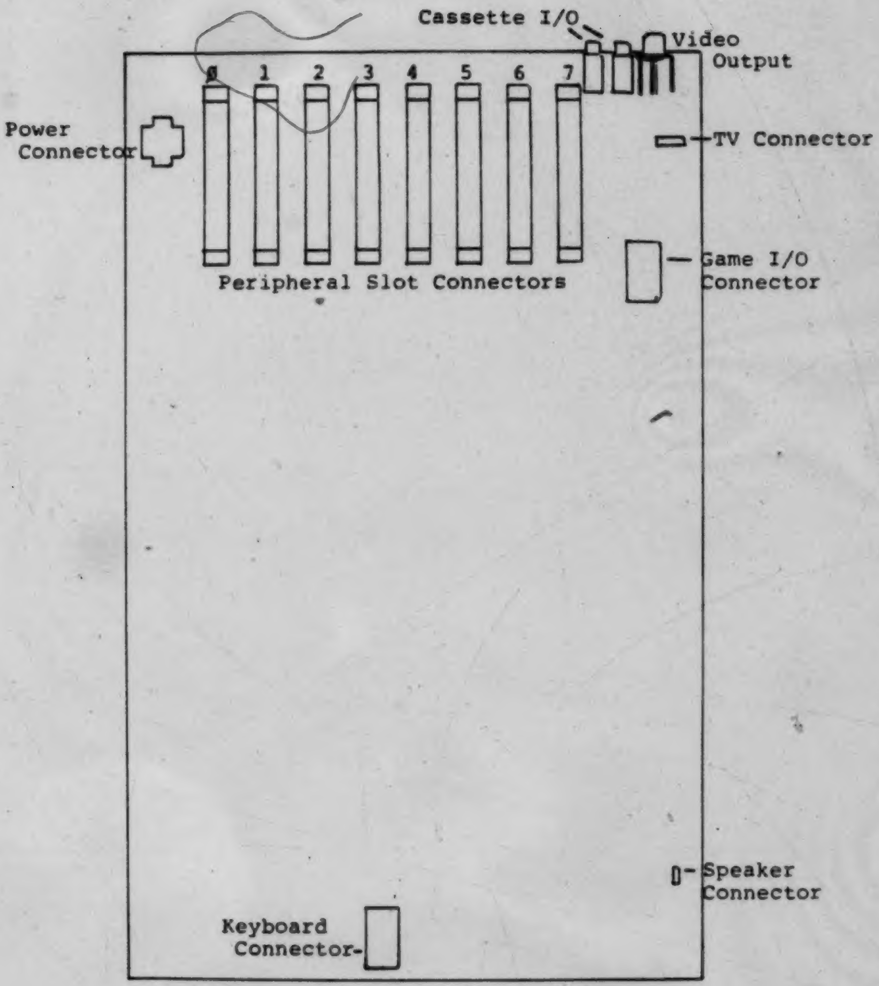

Cassette I/O
Video Output
0
1
2
3
4
5
6
7
Power Connector
TV Connector
Game I/O Connector
Peripheral Slot Connectors
Speaker Connector
Keyboard Connector

Figure 35. Input/Output connections on the Apple II+ main circuit board.

peripheral devices. The Apple has been commercially successful and there are a lot of reasonably priced peripheral devices available that can be plugged directly into the slot connectors.

The direct reader system has six of these eight slot connectors in use, as shown in Table 15.

Five of the six plugged in peripherals are commercial devices and are described below. The sixth is a custom built circuit to control the integration times of the array and is described in a separate section.

2.1 16k Byte Memory Expansion Board

This uses the same memory addresses as the Apple monitor and BASIC language read only memory (ROM). This restricts its usefulness. It is intended to be used to store a language interpreter as an alternative to the Applesoft floating point BASIC in ROM. When loaded with Integer BASIC, it has, as part of that language set, a restricted form of assembler language that is useful for writing programs for machine code operation.

This extra memory can be used to store machine language programs and binary data. It was considered for this purpose but diskette storage was found to be more convenient.

Table 15. System use of the peripheral slot connectors of the Apple II+.

SLOT	PERIPHERAL DEVICE
0	16k memory expansion board
1	Printer interface board
2	-
3	12-bit analog to digital converter
4	I/O board
5	Integration timer circuit board
6	-
7	Disc operating system controller

2.2 The Printer Interface Board

This is a GRAPPLER + by Orange Micro and it is interfaced to an Epson MX80FT dot matrix printer. The combination can print out information up to 80 characters wide and also give a printed copy of any high resolution graphics display on the video monitor.

2.3 The 12-Bit Analog to Digital Converter

This is an AI13 analog input system from Interactive Structures Inc. It has 16 software selectable analog input channels, 8 software selectable voltage ranges and a conversion time of 20 μs. On its lowest range (0 to 0.1 volts) the least significant bit (LSB) value is 0.024 mV, well below the 0.6 mV value for the 14-bit A/DC used with the AIM 65.

The AI13 is used in a mode that takes an externally generated high to low TTL transition as a trigger for conversion (the negative edge of the diode array RC1024S board's sampling pulse), and then generates an interrupt after conversion is complete.

Although the AI13 does not need a further preamplification stage for gain, it does require the analog inputs to be offset by means of a summing amplifier, in order to use its lower input voltage ranges. This is required to overcome the variation of the background level of the photodiode array with changes in integration time.

The amplifier shown in Figure 36 was built 6 times, once for each array. The operational amplifiers are LF351 from National Semiconductor Corporation and are of a similar type to the ones used previously. The AI13 takes its power off the Apple power supply (+11.8 V, -12 V, +5 V). The preamplifiers are also powered by the Apple to avoid any accidental overload of the AI13. The offset controllers are 10 turn precision wire wound potentiometers, equipped with turns counting dials. These were mounted on the side of the amplifier case to allow various offset voltages to be switched in quickly and reproducibly.

2.4 The Input/Output Controller Board

This is the DI09 I/O board from Interactive Structures. The controller contains two 6522 Versatile Interface Adapter (VIA) integrated circuits and has some partial address decoding. Thus it has four 8 bit parallel I/O ports with 8 control lines.

Only one 6522 is used by the system. The lower 3 bits of port A (PA0 to PA2) are used as inputs to read the encoded identity of a start pulse and determine which array is about to be read out. This identification is required so that the computer can select the correct input analog channel of the A/DC and select the correct data storage addresses. The upper 4 bits of port A (PA4 to

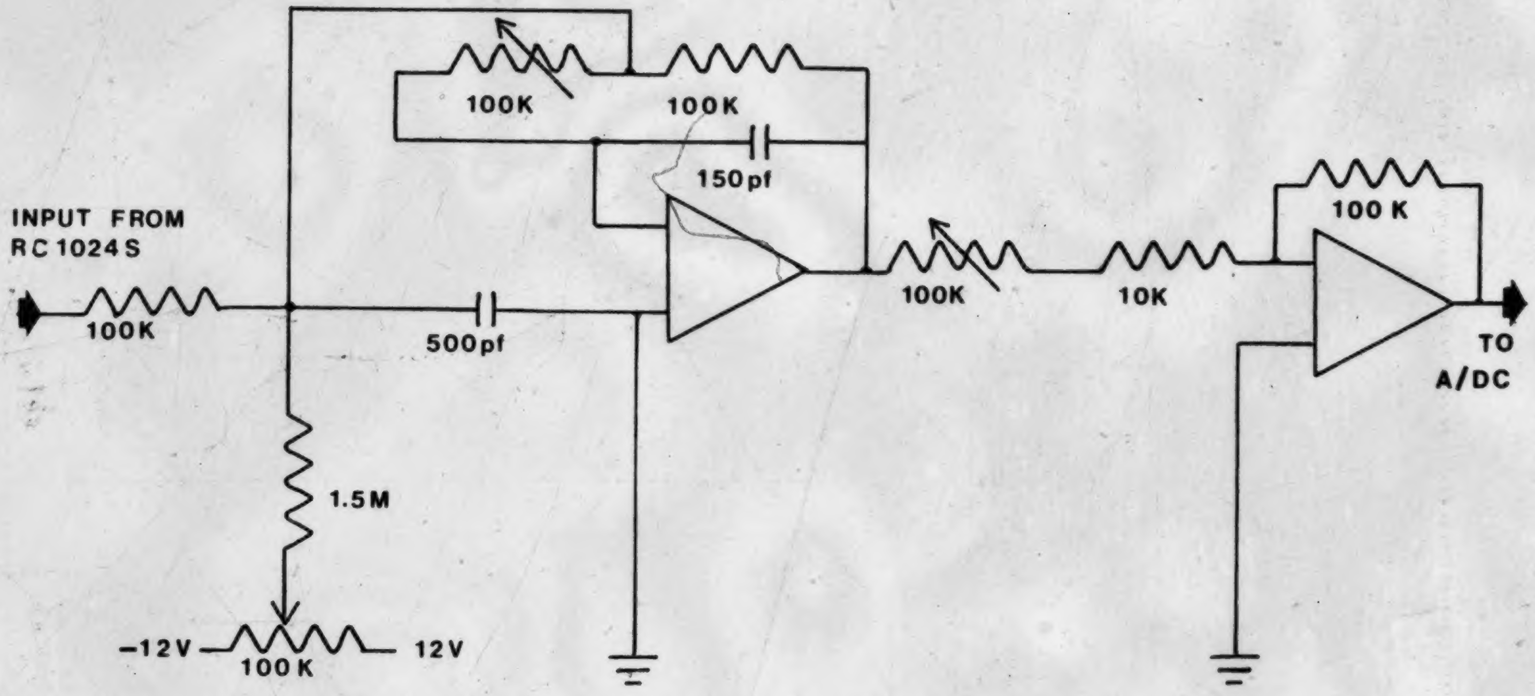

INPUT FROM
RC1024S
100K
100K
100K
150pf
500pf
1.5M
−12V
100K
12V
100K
10K
100 K
TO
A/DC

Figure 36. The preamplifier circuit for use with the AI13 A/DC.

PA7) and all bits of port B (PB0 to PB7) are used as outputs to load a digital to analog converter. This allows any data in the system to be displayed on an oscilloscope or graphed by a chart recorder.

For data collection, the I/O controller board has to detect both the rising and falling edges of the start pulse of the array about to be read out. This is done through control line CA1.

2.5 The Disc Operating System Controller

This supports 2 disk drives that use 5 1/4 inch diameter floppy disks. Drive No. 1 is usually loaded with the direct reader operating system disk. Drive No. 2 is used for data storage disks.

It has become normal practice with Apple computers to put this controller in slot 6, however, in this system it has been moved to slot 7 to relieve crowding around the integration timer circuit board in slot 5.

3. The Integration Timer System

3.1 The Timing and Sequencing Principle

In order to allow measurement of a wide range of emission intensities, the individual photodiode arrays must have independently variable integration times. In order to be processed by a single data logging system, the readout times of the arrays must not clash.

The degree of variability allowed to the integration time has to be restricted so that both of the above conditions can be met.

A short time interval, long enough for 6 arrays to be read out with a little time to spare, is selected as the standard integration time increment. All integration times are controlled to be integer multiples of this increment. Each individual array is allocated a fixed portion of the standard time increment during which it may be read out. When the integration timers start running, each one starts at the beginning of its allocated portion of the standard time increment. As the integration times are an integer multiple of the standard increment, the readout for each array has to occur within its allocated portion although probably many standard increments later. This prevents readout clashes as the allocated portions for different arrays are separated by enough time for complete readout of an array. This is illustrated in Figure 37.

The standard time increment is 0.1001 s made up of 32 pulses each of 3.129 ms. An array of 128 diodes takes 13 ms to be read out at a sampling rate of 10 kHz. Array 0 is allocated the first portion of the standard increment. Array 1 is allocated the portion beginning 5 pulses or 15.645 ms after the start of the standard

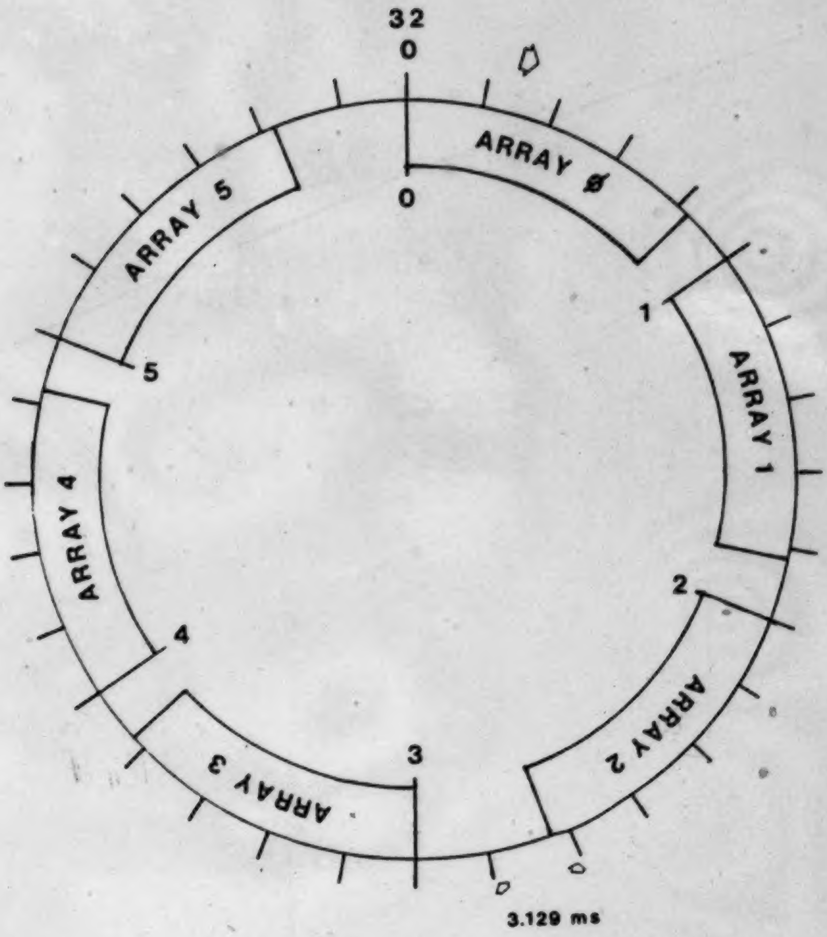

32
0
ARRAY 0
0
1
ARRAY 1
2
ARRAY 2
3
ARRAY 3
4
ARRAY 4
5
ARRAY 5
3.129 ms

Figure 37. The integration timer cycle.

increment. Array 2 is allocated the portion starting 10 pulses after the start of the increment, and so on.

The integration times of each array have to be multiples of .1001 s. This also means that the minimum integration time is .1001 s, and this suggests that less prominent spectral lines may have to be used to analyze high concentrations of some elements to avoid saturation of the photodiode array.

It would be extremely difficult for the central processing unit of the computer to act as the timing device. It would have to run six counting loops and after it broke away from the counting loops to process the data from an array, it would have to correct the timing for the other five arrays and restart the loop for the one just read out.

The more convenient method chosen uses software to load the integration times onto a series of timers that then run independently of the central processing unit. The central processing unit idles in a loop until it responds to the rising edge of a start pulse generated by one of the integration timers. After processing the corresponding array readout it returns to the idling loop until the next start pulse occurs.

3.2 Design and Construction of the Timing Device

The timer system and its associated integrated circuits were assembled on an Apple peripheral prototyping printed circuit board. The logic diagram for this assembly is shown in Figure 38.

The primary oscillator of the Apple is a 14.31818 MHz quartz crystal. This frequency is reduced to 1.023 MHz to clock the central processing unit and this same reduced frequency is also made available at the peripheral slot connectors.

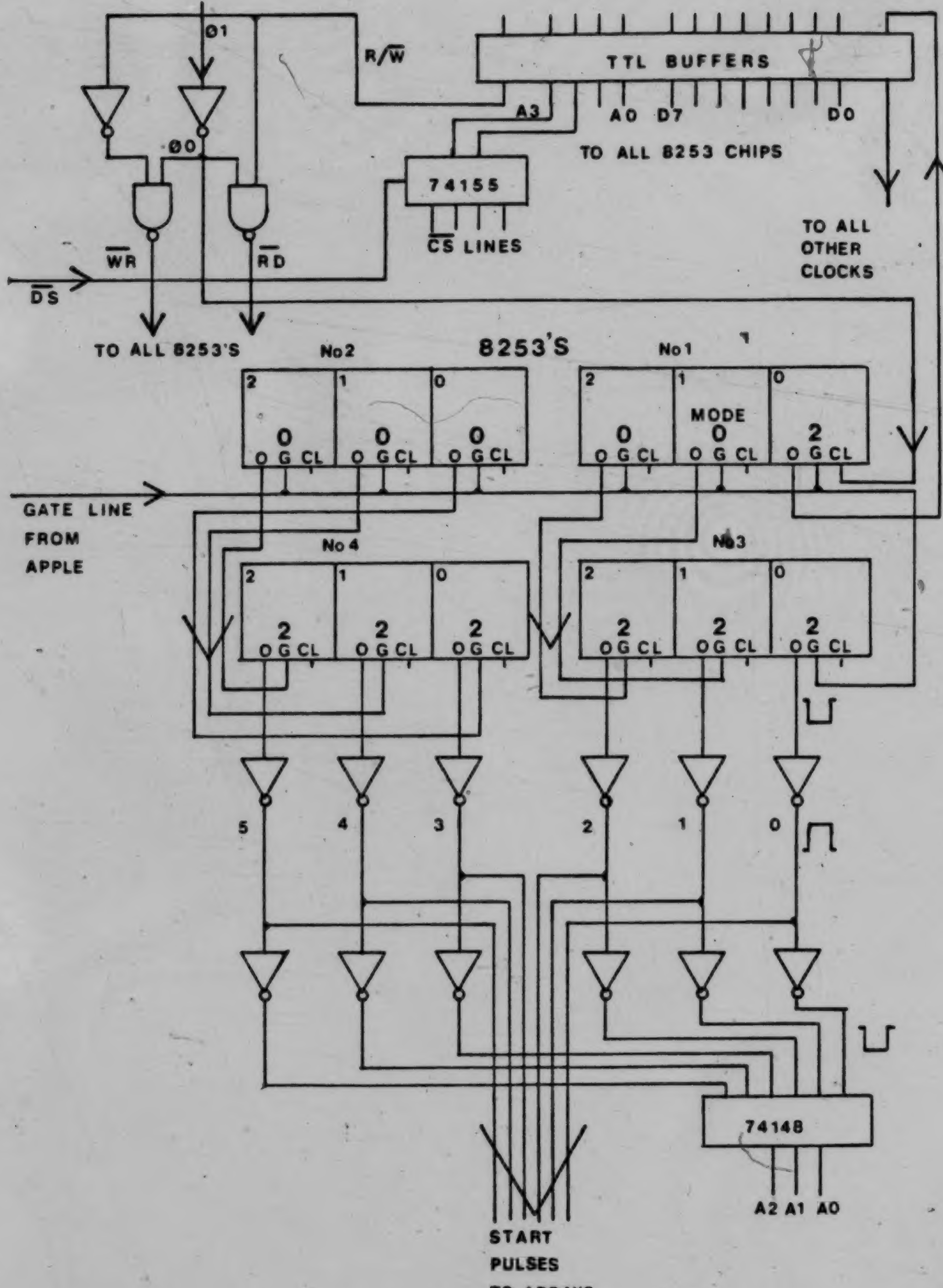
The heart of the integration timing system consists of four 8253 integrated circuit chips. Each of these has three 16-bit programmable down counters that can run independently of each other in any one of six modes and this supplies the 12 counters necessary to run the system.

The 12 counters are utilized as follows:

i. One is used to reduce the time base clock frequency by a factor of 3,200 (to give a period of 3.129 ms) and this is used to drive the other eleven counters.

ii. Five are used to control the gating of five of the integration counters to delay the start of their counting cycles by fixed amounts of time.

iii. Six act as the actual integration timers. These are loaded with the integration times for each individual array as selected by the operator of the direct reader.



Ø1
R/W
TTL BUFFERS
A3
A0
D7
D0
TO ALL 8253 CHIPS
Ø0
74155
CS LINES
TO ALL OTHER CLOCKS
WR
RD
DS
TO ALL 8253'S
No2
8253'S
No1
2
1
0
MODE
O G CL
GATE LINE FROM APPLE
No4
No3
5
4
3
2
1
0
74148
A2 A1 A0
START PULSES TO ARRAYS

Figure 38. The integration timer circuit logic.

The power supply for the Apple has only 500 mA available at 5 V for all the eight peripheral slot connectors. As the four 8253 integrated circuits alone draw 560 mA the timer circuitry was driven by an auxiliary power supply.

The data bus and part of the address bus of the microcomputer have to go to all four 8253 chips. In order to avoid fan-out problems, the bus lines and the READ/$\overline{\text{WRITE}}$ control line were first buffered through 74125 tri-state buffers.

The circuit requires the $\phi 0$ signal from the computer. This is the phase of the computer clock signal that goes high for data transfer. Because this signal has considerable fan-out on the Apple main board, it was recreated for the timer circuit by inverting its complement $\phi 1$.

For an added complication, the 8253 chips are not designed for use with the 6502 microprocessor that drives the Apple. They are designed for use with Intel's 8080 microprocessor. The essential difference between the two is that the 8080 has separate read and write control lines, while the 6502 uses a single line for both read and write control. When this line is high and $\phi 0$ is high, the 6502 reads data. When the line is low and $\phi 0$ high, the 6502 writes (outputs) data. A special interface has been designed by V. Karanassios [48] to allow the 8253 and similar Intel chips to be used on 6502 based equipment and this was incorporated into the circuit.

Because the data bus was buffered through one way tri-states, the status of the count in progress could not be read out through the data bus. This does not matter as the timer output pins carry the end of count signals.

3.3 Addressing the Counters

The counters within the 8253 chips have to be individually programmed and this requires that they be individually addressed. The circuit board runs in slot 5 which has the dedicated address $C0D0 to $C0DF ($ = hexadecimal symbol). When any of these 16 addresses is referenced a control line at the slot interface goes low for 500 ns. This is called the $\overline{DS}$ (Device Select) pulse for that slot.

Consider the last hexadecimal digit of these 16 addresses expanded to its four binary address lines A3, A2, A1 and A0. Address lines A3 and A2 are fed to a 2 line to 4 line decoder (74155) which is activated by the $\overline{DS}$ pulse. The four outputs from the 74155 are used as $\overline{CS}$ (chip select) pulses and are fed individually to the four 8253 chips. Thus the particular chip being addressed is controlled by the values of A3 and A2. The A1 and A0 address lines go to all 8253 chips where they are used to address the individual counters or to signify the transfer of control information (mode word). The full address list for write instructions to the system is given in Table 16.

In order to synchronize the start of the counting operations, the counters are inactivated during the data loading process. This is done by holding the gates of the frequency reduction and delay counters low (disable) with a software controlled logic level through the Apple game I/O connector. When all the counters are loaded the logic level is software switched to high, the gates are opened (enabled) and the count operations commence.

The timing diagrams for the counting processes are given in Figure 39.

Counter 0 on 8253 #1 runs in mode 2 as a frequency reducer. It is loaded with a count for 3,200 and clocked by the 1.023 MHz Apple drive frequency. The output is normally high but every 3,200 clock cycles or 3.129 ms it goes low for 1 µs. The reduced frequency output signal is buffered through a 74125 tri-state and then is fed to the other eleven counters in the system.

Counters 1 and 2 on 8253 #1 and all three counters on 8253 #2 are run in mode 0 as interrupt timers. The outputs go low as the counter register is loaded. When the count starts the output remains low until full count occurs, whereupon it goes high and stays high until the

Table 16. The address list for loading the integration timer system.

ADDRESS (HEX CODE)	8253 ADDRESSED	EFFECT OF WRITE INSTRUCTION
$C0D0	1	LOAD COUNTER #0
$C0D1	1	LOAD COUNTER #1
$C0D2	1	LOAD COUNTER #2
$C0D3	1	WRITE MODE WORD
$C0D4	2	LOAD COUNTER #0
$C0D5	2	LOAD COUNTER #1
$C0D6	2	LOAD COUNTER #2
$C0D7	2	WRITE MODE WORD
$C0D8	3	LOAD COUNTER #0
$C0D9	3	LOAD COUNTER #1
$C0DA	3	LOAD COUNTER #2
$C0DB	3	WRITE MODE WORD
$C0DC	4	LOAD COUNTER #0
$C0DD	4	LOAD COUNTER #1
$C0DE	4	LOAD COUNTER #2
$C0DF	4	WRITE MODE WORD

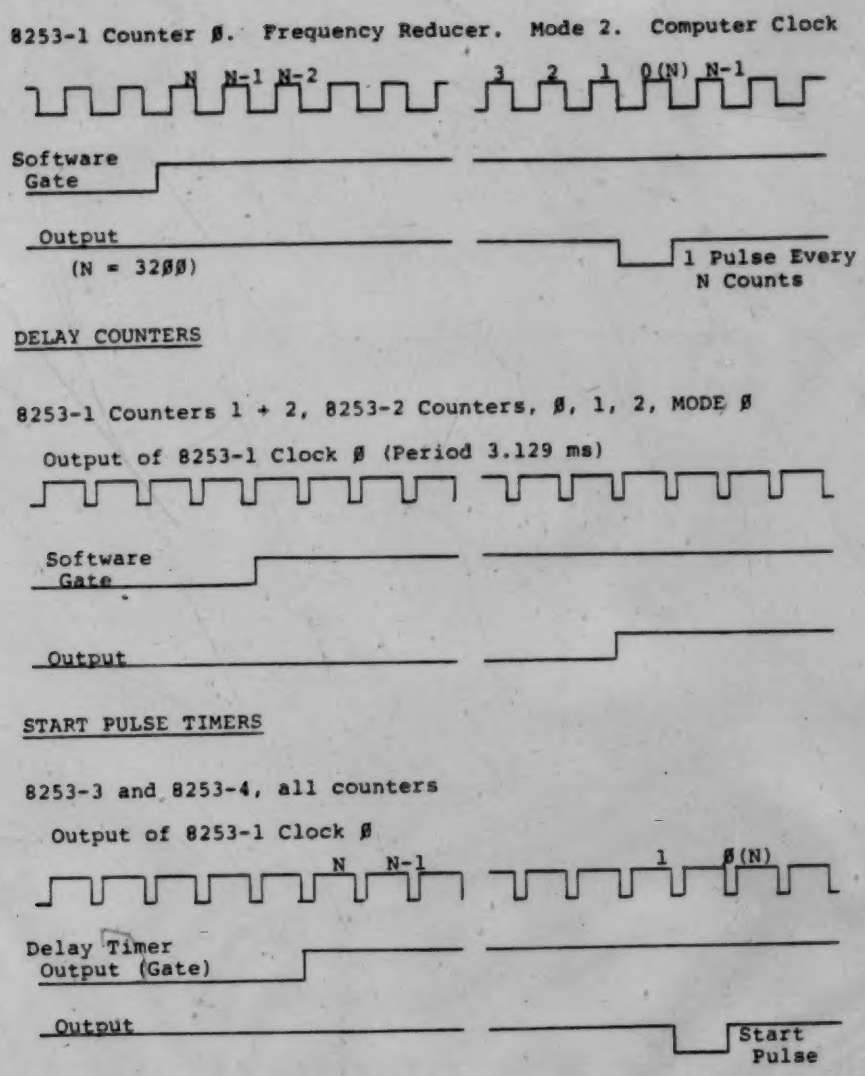

8253-1 Counter 0. Frequency Reducer. Mode 2. Computer Clock
N N-1 N-2
3 2 1 0(N) N-1
Software Gate
Output
(N = 3200)
1 Pulse Every N Counts
DELAY COUNTERS
8253-1 Counters 1 + 2, 8253-2 Counters, 0, 1, 2, MODE 0
Output of 8253-1 Clock 0 (Period 3.129 ms)
Software Gate
Output
START PULSE TIMERS
8253-3 and 8253-4, all counters
Output of 8253-1 Clock 0
N N-1
1 0(N)
Delay Timer Output (Gate)
Output
Start Pulse

Figure 39.

Timing diagrams for the 8253 software programmable counters.

count register is reloaded. As this only occurs when all the counters are being loaded, once the output has gone high it stays high for the duration of all of the counting operations. The outputs of these 5 counters are used to gate 5 of the integration timer counters. They are loaded with sufficient counts to hold their outputs low for the delay intervals required to sequence the integration timers.

The six counters on 8253 #3 and #4 run in mode 2 as frequency reducers. They are loaded with counts that generate pulses at periods corresponding to the required integration times. At the completion of each count a negative pulse 3.129 ms wide is generated as a start pulse. As the counters are 16-bit, they can count up to 65,536 pulses of 3.129 ms and this gives a maximum integration time of 205 s.

3.4 Further Processing of the Start Pulse

The negative start pulse is inverted to a positive one and fed out to the appropriate diode array RC1024S control board. It opens the gate for the control board oscillator and also clocks the onboard flip-flop (Figure 18) so that its output goes high.

The pulse is also reinverted and sent to a 74148 priority encoder. This detects which start pulse has occurred and translates this information into a code that is the binary equivalent of the number identifying the array to be read out. This code is fed to the Apple computer through the PA0 to PA2 inputs on the DI09 input/output controller board.

The computer program for data acquisition requires that the identity of the array be generated in straight binary. Reference to the truth table (Table 17) indicates that if the start pulse for diode array 0 were fed to input 0 on the 74148, it would generate binary 1,1,1 at the outputs A2, A1, A0. This is the 1's complement of the 0,0,0 required. The outputs from the 74148 could be inverted but the printed circuit cannot hold another integrated circuit chip. The correct coding at the outputs is obtained by connecting reinverted start pulse 0 to input 7 on the 74148, 1 to 6, etc.

The input enable is grounded so that the 74148 is always operating when the power is on. For most of the integration period the outputs will be high but this is immaterial as the computer only samples them after a start pulse has been received.

The integrated circuit chip layout for the integration timer board is given in Figure 40. Sockets A and B are wired in parallel. A plug into A transfers the generated start pulses to the leads to the diode array control boards. It also brings in the OR'd sampling

Table 17. Truth table for 74148 priority encoder. (H = High logic level, L = Low logic level, X = Either)

INPUTS									OUTPUTS				
EI	0	1	2	3	4	5	6	7	A2	A1	A0	GS	E0
H	X	X	X	X	X	X	X	X	H	H	H	H	H
L	H	H	H	H	H	H	H	H	H	H	H	H	L
L	X	X	X	X	X	X	X	L	L	L	L	L	H
L	X	X	X	X	X	X	L	H	L	L	H	L	H
L	X	X	X	X	X	L	H	H	L	H	L	L	H
L	X	X	X	X	L	H	H	H	L	H	H	L	H
L	X	X	X	L	H	H	H	H	H	L	L	L	H
L	X	X	L	H	H	H	H	H	H	L	H	L	H
L	X	L	H	H	H	H	H	H	H	H	L	L	H
L	L	H	H	H	H	H	H	H	H	H	H	L	H

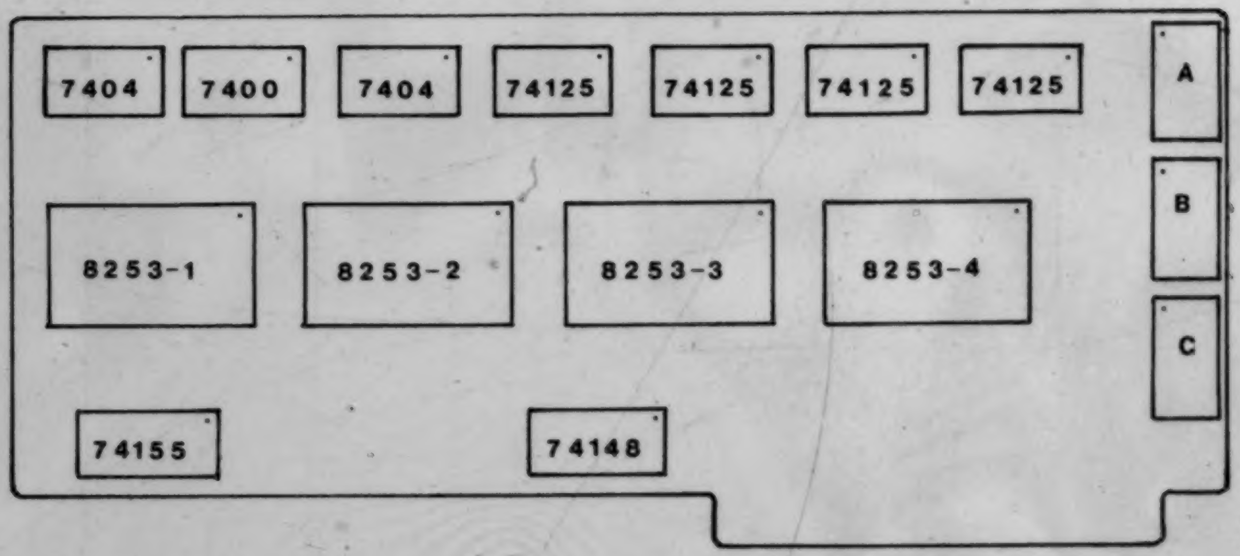

7404
7400
7404
74125
74125
74125
74125
A
B
C
8253-1
8253-2
8253-3
8253-4
74155
74148

Figure 40. Chip layout of the integration timer circuit board.

pulses and start pulses back from the array control boards (discussed in section 4 of this chapter).

A plug into B transfers the start pulses to an LED display (discussed in section 5 of this chapter). This plug also acts as a connector for the transfer of the OR'd sampling pulses to the trigger of the analog to digital converter (section 2.3 of this chapter) and of the OR'd start pulses to control line CA1 on the DI09 input/output controller board. Socket C is connected to the A2, A1, A0 outputs of the 74148 priority encoder. A plug in C carries these lines to the PA0 to PA2 inputs on the DI09.

4. Timing Signals Required by the Computer

The Apple computer uses the timing signals from the array board differently to the way they were used by the AIM 65 for a single array. The computer must identify the array about to be read out so that it can switch the A/DC to the correct analog channel and set up the correct storage addresses for the data.

During data acquisition the integration timer system runs independently of the microprocessor. The first indication that an array is about to be read out is the leading positive edge of the start pulse (see Figure 17). This clocks the 7474 flip-flop on the RC1024S board (Figure 18), sending its Q output high. The Q outputs on the boards for all 6 arrays are logically OR'd together and the resulting single line fed to the computer through control line CA1 on the I/O board. The computer reacts to this low to high transition, reads the identity of the array from the 74148, and sets up the A/DC input channel and the correct addresses in the data storage program. It has less than 200 μs to do this before the Q output is cleared to low by the Ø2 ODD pulse.

The sampling pulses for all of the arrays are likewise logically OR'd together and the resulting single line fed as a trigger to the A/DC. As with the AIM, the first diode read out corresponds to the first sampling pulse received after the Q output of the flip-flop is cleared to low. The diagram for the circuit to OR the signals is shown in Figure 41.

The computer detects the edges of the OR'd start pulses returned from the array boards, not those of the pulses generated by the timer circuit board. Consequently, it does not matter that the latter are active for 3.129 ms. They will be inactive well before the next start pulse is generated.

With the single array system the sampling pulse was fed to the A/DC and the conversion completed signal was used by the AIM as a cue to read the data values. The AI13 operates differently. The A/DC operates under the

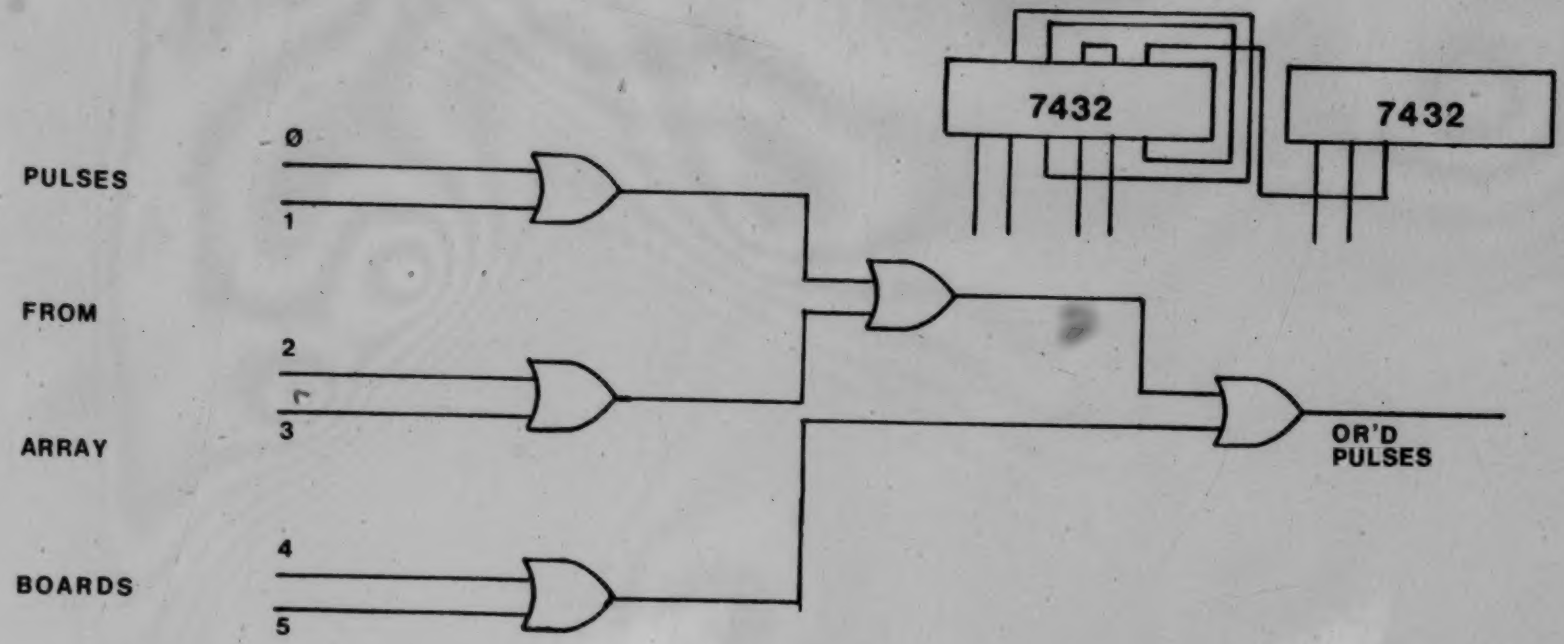

7432
7432
PULSES
FROM
ARRAY
BOARDS
0
1
2
3
4
5
OR'D
PULSES

Figure 41. Logic to OR the start or sample pulses of all six arrays.

control of the computer which has to supply the identity of the analog channel and the A/DC range setting. The actual conversion occurs after a negative edge trigger (the sampling pulse) and the computer polls the high byte address of the A/DC for the signal that indicates the completion of the conversion before reading the data values. This slightly lengthens the time to read out a single diode but the length of the diode readout loop still remains less than the 100 μs limit required by a 10 kHz readout rate.

5. Auxiliary Circuits

5.1 A Start Pulse Indicator

After a change has been made in the analyte aspirating into the plasma nebulizer, all of the diode arrays must be cleared by completing their current integration period before valid data can be taken. If this is not done the data would be spurious. It is very easy to lose track of the integration state of 6 arrays and excessive delay wastes time. A start pulse indicator was built as an operating aid to keep track of the clearing arrays. The circuit diagram is shown in Figure 42.

As a start pulse occurs, it clocks a 7474 flip-flop and sends its Q output high and the complementary $\overline{Q}$ output

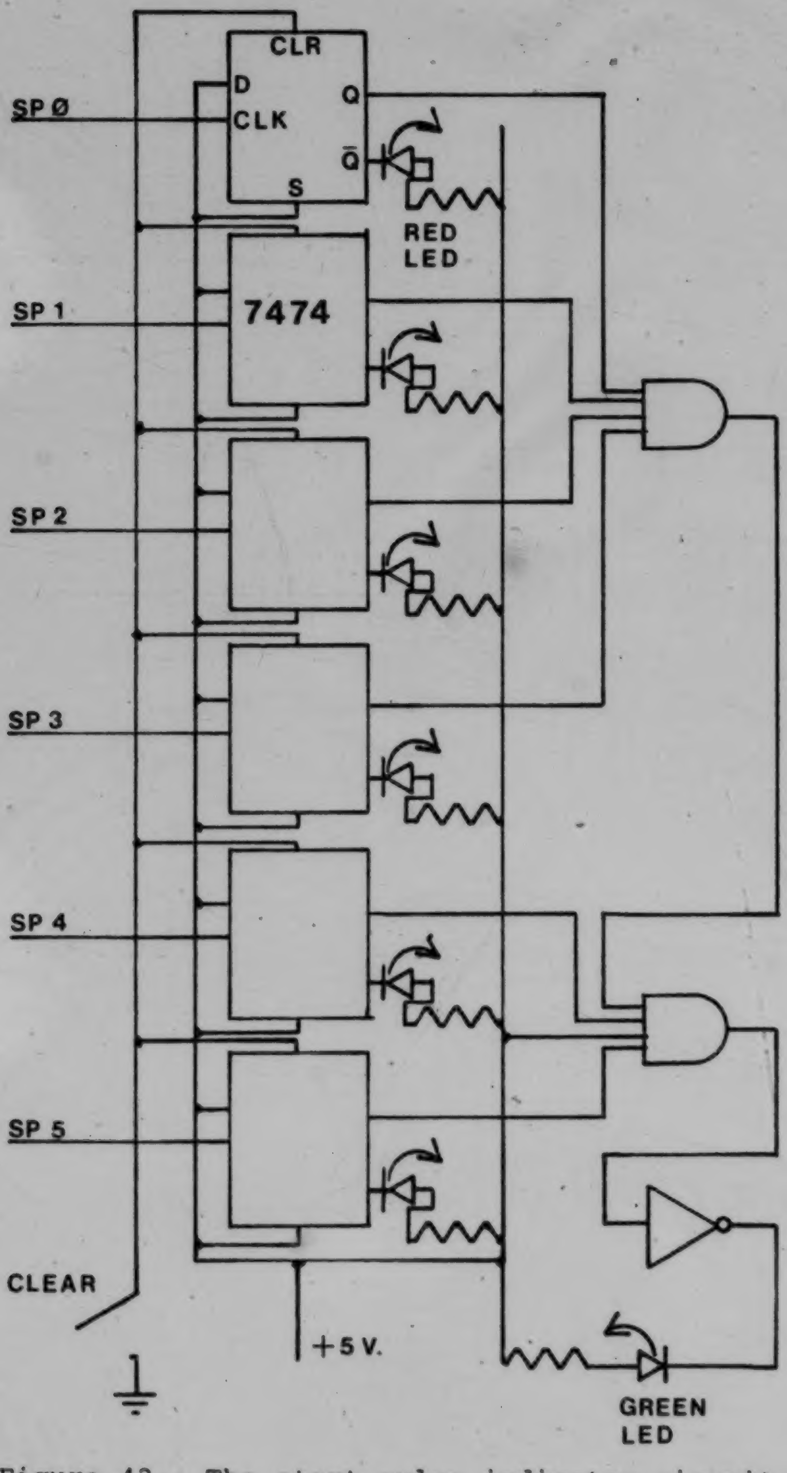

CLR
D
Q
SP Ø
CLK
Q̄
S
RED
LED
SP 1
7474
SP 2
SP 3
SP 4
SP 5
CLEAR
+5 V.
GREEN
LED

Figure 42. The start pulse indicator circuit.

low. The low $\overline{Q}$ forward biases a red LED so that it lights up.

The Q outputs for all 6 flip-flops are combined through AND gates so that a high logic level state occurs after all the arrays have received at least one start pulse. This high level is inverted to a low level that forward biases a green LED causing it to light up.

When the operator has made an analyte change and is satisfied that the plasma emission has restabilized, he presses a button that clears all of the flip-flops. Their $\overline{Q}$ outputs go high and all the LEDs go out. As the arrays complete their next integration cycle, their corresponding red LEDs light and when all reds are lit the green also lights as a signal to the operator to start the data acquisition process.

5.2 Output to a Chart Recorder or Oscilloscope

It is very useful to be able to display a digitized, recorded spectrum on an analog device such as a chart recorder or an oscilloscope. This requires reconversion of the digitized signal to an analog one through a digital to analog converter (D/AC). The circuit diagram is shown in Figure 43.

The computer has an 8-bit data bus and so must process and store 12-bit data in two bytes. When the data fed to the D/AC is to be changed, it must be changed at

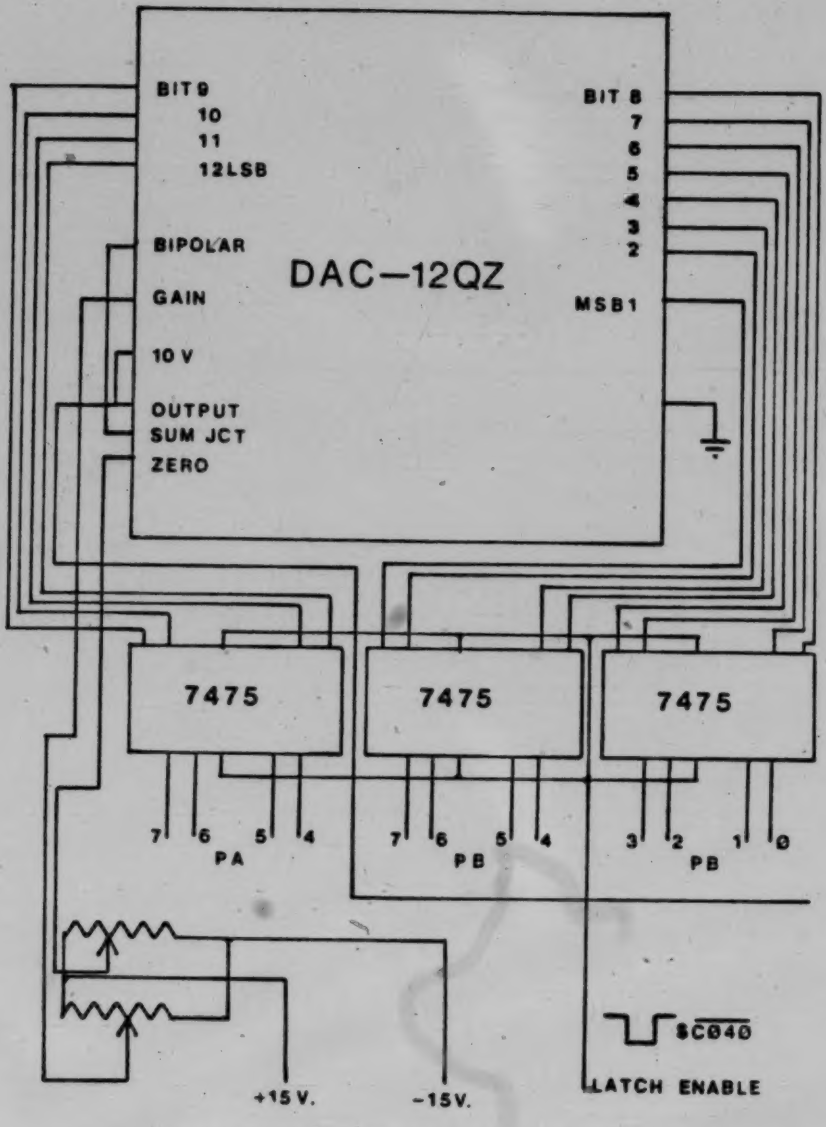

BIT 9
10
11
12LSB
BIPOLAR
GAIN
10 V
OUTPUT
SUM JCT
ZERO
DAC—12QZ
BIT 8
7
6
5
4
3
2
MSB1
7475
7475
7475
7
6
5
4
PA
7
6
5
4
PB
3
2
1
0
PB
$C040
+15 V.
−15V.
LATCH ENABLE

Figure 43. The digital to analog conversion circuit.

all D/AC inputs simultaneously. This is achieved by loading the output from the computer onto the inputs of 7475 latches. The latches are then all enabled simultaneously so that the data at their inputs is transferred to their outputs and on to the D/AC inputs.

The digital signal is put out through the PB0 to PB7 and PA4 to PA7 ports of the D109 input/output controller which are dedicated to this task. (The lower ports PA2 to PA0 are dedicated to the input of the array identity code.) This means that both bytes of the data values have to be software shifted 4 bits higher in the data buffer prior to loading the D/AC.

A diagram showing the interrelationship of the circuitry built external to the direct reader light proof box is given in Figure 44.

Inside the light proof box, all digital and analog signals are carried as far as is practical by coaxial cable to prevent cross-talk. Outside the box, the analog signals are carried by coaxial cable as far as the preamplifier. Digital signals are carried by VARI-TWIST flat cable between the light proof box and the Apple computer.

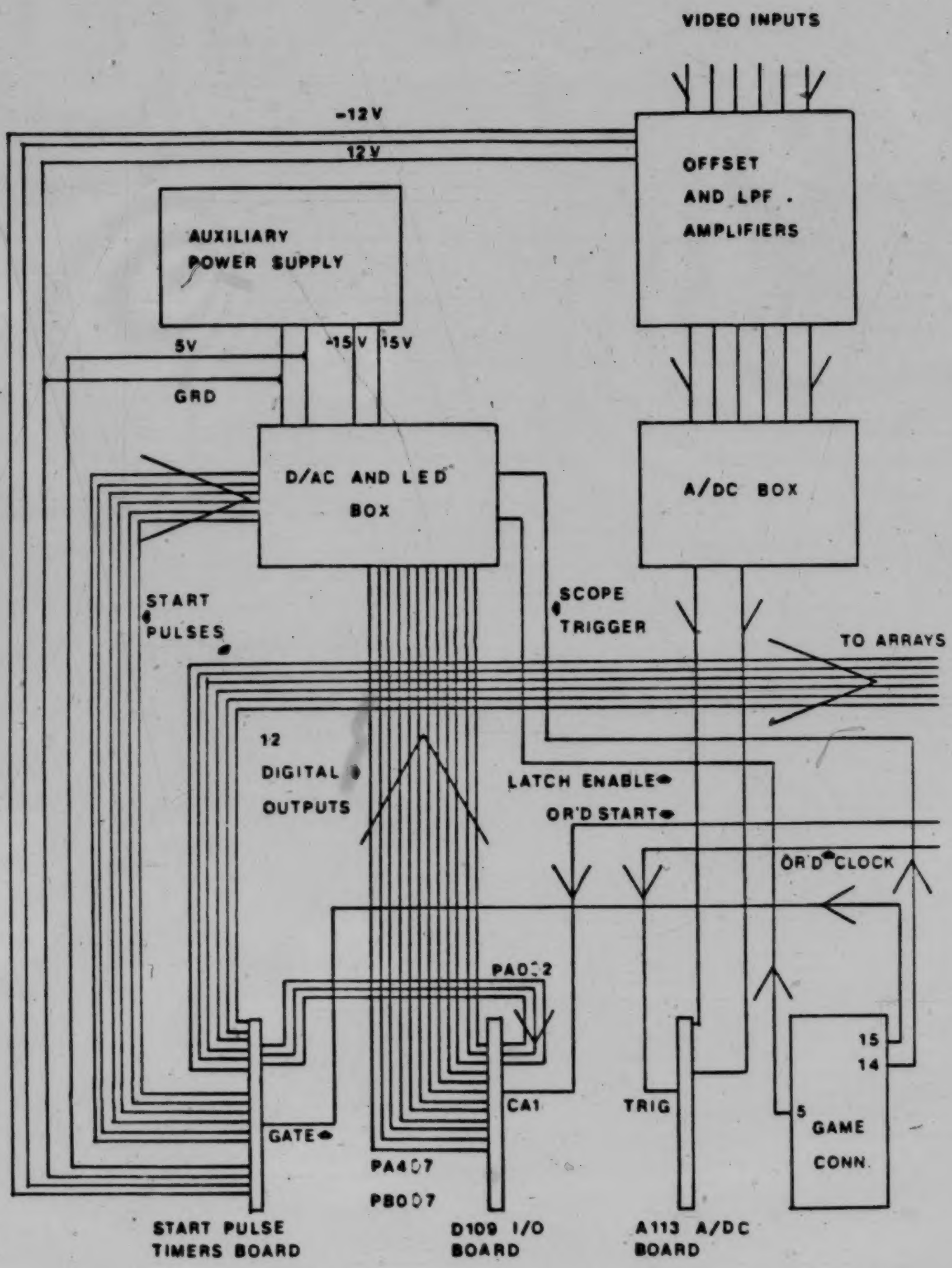

VIDEO INPUTS
-12V
12V
OFFSET AND LPF. AMPLIFIERS
AUXILIARY POWER SUPPLY
5V
-15V
15V
GRD
D/AC AND LED BOX
A/DC BOX
START PULSES
SCOPE TRIGGER
TO ARRAYS
12 DIGITAL OUTPUTS
LATCH ENABLE
OR'D START
OR'D CLOCK
PA002
GATE
CA1
TRIG
15
14
5
GAME CONN.
PA407
PB007
START PULSE TIMERS BOARD
D109 I/O BOARD
A113 A/DC BOARD

Figure 44. General diagram of circuitry outside the direct reader lightproof box.

6. The Computer Operational Plan

The Apple computer uses 2 byte or 16-bit addressing and so can reference any of 65,536 memory locations. This may seem like a lot but a considerable portion of it is already committed to operating systems and language interpretation. That portion still available is not sufficient to hold all of the necessary programs and store the acquired data from 6 arrays.

Because of this memory shortage, a system is used that makes extensive use of disk storage. This is based on the Disk Operating System (DOS) of the computer and the ease of inclusion of DOS commands within a BASIC program.

A master program, written in BASIC, displays a menu on the video monitor and allows the operator to call up other BASIC programs from the disk. These secondary programs control the various operations required, calling up other programs written in BASIC or machine code as needed. For high speed operation, data logging and control functions are carried out by machine language programs with BASIC used to communicate with the operator.

6.1 Organization of the Apple Memory Space

The memory space allocation is shown in block form in Table 18. With disk operating system booted, about half of the memory addresses are allocated to specific uses.

Table 18. Memory space utilization of the Apple II+.

HEX	ADDRESS	MEMORY FUNCTION	
FROM	TO		
D000	FFFF	BASIC AND MONITOR	ROM
C000	CFFF	I/0 RESERVED SPACE	
9600	BFFF	D.O.S. RESERVED SPACE	RAM
7300	95FF	BINARY STORAGE AND MACHINE CODE PROGRAMMING SPACE	RAM
4000	72FF	BASIC PROGRAMMING SPACE	RAM
2000	3FFF	HIGH RESOLUTION GRAPHICS PAGE 1 STORAGE	
0800	1FFF		
0400	07FF	VIDEO SCREEN TEXT SPACE	RAM
03F0	03FF	VECTOR STORAGE SPACE	RAM
0300	03EF	AVAILABLE MACHINE CODE SPACE	RAM
0200	02FF	KEYBOARD INPUT BUFFER	RAM
0100	01FF	SYSTEM STACK	RAM
0000	00FF	ZERO PAGE	RAM

In order to run both BASIC and machine code programs a bank of addresses had to be reserved for machine code and binary storage. The memory addresses between $72FF and $95FF were reserved by starting all BASIC programs with the statement HIMEM:29439 ($72FF in hexadecimal). This prevents BASIC use of the addresses above $72FF. $9600 is the lowest address used by the DOS.

The machine code and binary storage memory was subdivided as shown in Table 19.

Whenever a machine code program is called from disk, it is loaded into the memory space that begins at $9200. The scratch pad memory addresses are individually allocated as listed in Appendix 5. Operating parameters are called for by BASIC programs and then stored in the scratch pad area using the BASIC POKE statement. They are then read and utilized by machine code programs.

The binary storage memory accommodates 4 files. Newly acquired data for all arrays (768 diodes) is stored as received in the buffer file in real time. It can then be relocated, if necessary, to the background raw data storage file. The analyte and background means files are used to store the mean (signal averaged) data values calculated through a BASIC program from the accumulated values in the other files. The availability of several storage files in RAM allows background subtraction and other spectrum stripping techniques to be used.

Table 19. Utilization of protected machine code and binary data memory space.

HEX ADDRESS FROM	TO	MEMORY FUNCTION
9200	95FF	MACHINE CODE PROGRAMMING SPACE
8900	91FF	BACKGROUND RAW DATE FILE
8000	88FF	INPUT BUFFER (DATA FILE)
7F01	7FFF	SCRATCH PAD MEMORY SPACE
7900	7EFF	ANALYTE MEANS FILE
7300	78FF	BACKGROUND MEANS FILE

6.2 Programming

When the computer is booted with a disk loaded with the direct reader operating system programs, the main menu, shown in Figure 45, appears on the video monitor.

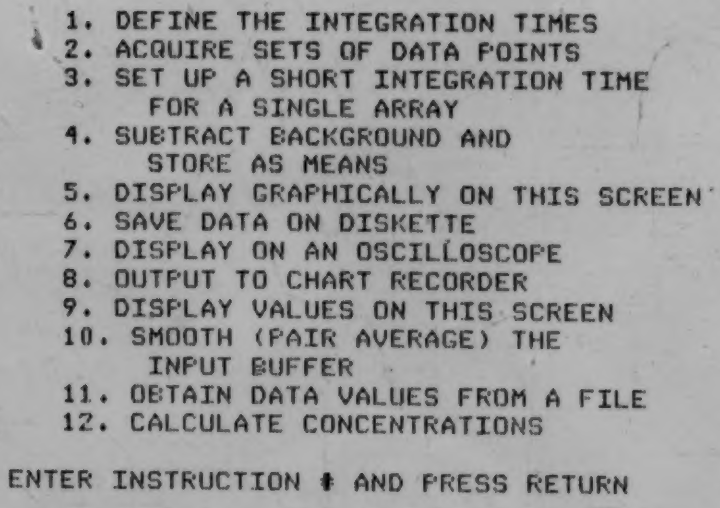
The various options listed can be called up through the master program by entering the selection number, or called directly from the disk by the DOS command RUNSEL followed by the number.

All of the programming techniques are described and the programs listed in Appendix 6. Their general functions are briefly described here.

6.2.1 1. Define the Integration Times

The program asks for the integration time for each of the 6 arrays. The entered values are corrected to valid values and entered into scratch pad addresses. The machine code part of this program then loads the necessary count values into the 8253 counters on the integration timer circuit board and starts the integration cycles.

The RESET key on the Apple cancels the operation of the integration timer board but does not affect the data stored in scratch pad memory. To save time, a quick reload option (no data entry required) is included in this program.



```
  1. DEFINE THE INTEGRATION TIMES
  2. ACQUIRE SETS OF DATA POINTS
  3. SET UP A SHORT INTEGRATION TIME
       FOR A SINGLE ARRAY
  4. SUBTRACT BACKGROUND AND
       STORE AS MEANS
  5. DISPLAY GRAPHICALLY ON THIS SCREEN
  6. SAVE DATA ON DISKETTE
  7. DISPLAY ON AN OSCILLOSCOPE
  8. OUTPUT TO CHART RECORDER
  9. DISPLAY VALUES ON THIS SCREEN
  10. SMOOTH (PAIR AVERAGE) THE
       INPUT BUFFER
  11. OBTAIN DATA VALUES FROM A FILE
  12. CALCULATE CONCENTRATIONS

ENTER INSTRUCTION # AND PRESS RETURN
```

Figure 45. The direct reader operating system main menu.

6.2.2 2. Acquire Sets of Data Points

This program requires two input parameters for every array. These are the gain code to set the range for the AI13 analog to digital converter and the number of replicate runs to be taken for signal averaging. Again there is a quick load option (no data entry) but in this case it is to keep the parameters constant for a series of analytical runs. The machine code portion of the program is rather complicated as it involves control of the A/DC and storage address selection as well as data logging.

6.2.3 3. Set Up a Short Integration Time for a Single Array

This is a variation of selection 1 and is used to control the integration time of a single array during the setting up and tuning of the array system. It allows integration times as short as 0.018 s for a single array while the other 5 have an integration time of 205 s. It can also be used to collect data values for a very intense spectral emission that would saturate the array if run at the 0.1001 s minimum integration time allowed by selection 1.

6.2.4 4. Subtract Background and Store as Means

This program subtracts one set of spectral values from another; if necessary, it calculates mean values first. It can accept data in raw form or as precalculated means. The data can be in the computer's RAM or stored on disk. The main purpose is to subtract the background due to dark current or the spectrum of aspirated water from an analyte spectrum.

6.2.5 5. Display Graphically on This Screen

This is a BASIC program that presents the data for any single photodiode array in graphical form on the video screen. The axes of the display are labelled with the voltage range of the A/DC, the diode numbers and the array number. The resolution of the photodiode signal intensity is only to 7-bit (1 in 128) but it is very useful for detecting major spectral interferences and the condition of the background. There is provision for the addition of a title and the graph can be printed out.

6.2.6 6. Save Data on Diskette

The contents of any binary data file can be saved on a disk in drive 2. Two files are saved with a single instruction. One is the binary data file and the other corresponds to the portion of scratch pad memory that contains the parameters used to collect the data.

6.2.7 7. Output to an Oscilloscope

The data stored in the input buffer are displayed on an oscilloscope.

6.2.8 8. Output to a Chart Recorder

The data stored in the input buffer are fed out to a chart recorder. The output rate can be controlled to suit the response speed of the recorder pen.

6.2.9 9. Display Values on This Screen

The program calculates and displays the data values for all or a selected group of diodes on any array. The values are displayed as voltages and can be printed out.

6.2.10 10. Smooth (Pair Average) the Input Buffer

The ODD-EVEN pattern of the diode array signal is a considerable problem. Other workers have read the diodes out in pairs to avoid this [30]. Another approach has been to smooth out the signal by use of a notched filter set at a frequency below that of the diode sample pulse rate [49]. Both of these approaches lose some of the spectral resolution obtained from the use of the diode array. This program achieves the same object through software but retains more data points and hence loses less resolution.

6.2.11 11. Obtain Data Values from a File

The program evaluates the background near a specified spectral feature on any diode array and uses the background value to correct the peak height. The operator can control the selection of the diode values used to.

calculate the background to suit the interferences present on the array.

6.2.12 12. Calculate Concentrations

The program allows the calculation of the concentrations of several analytes from their peak heights by linear interpolation between values for calibration standards.

In addition to the direct reader system programs, two more have been written to assist in the placement of arrays. These are on a separate disk which also contains a set of text files compiled from the table of prominent lines in the ICP published by Winge, Peterson and Fassel [43]. The program ARRAYSET allows the compilation of a text file containing the prominent lines of selected elements in up to three spectral orders. These are sorted into wavelength order by means of a very fast machine code order sorting program developed by Bongers [50]. The list can be displayed and printed out for use as an aid in the selection of diode array positions along the focal plane. The program LINELOC converts the spectral position (wavelength multiplied by order) to a window position along the focal plane of the direct reader. An example of the use of these two programs is given in Chapter VI.

7. Engineering Considerations

The operation of six arrays in a confined space required careful planning of the services to each array. Because the positions of the arrays had to be adjustable over a wide range of distance along the focal plane of the direct reader, all service lines had to be flexible and arranged so that they could be kept in an orderly fashion. Services had to be obtained from available sources and supplied through distribution systems so that all of the arrays received the same quality of supply.

7.1 Cooling Considerations

The photodiode arrays require cooling to reduce their integrated dark current. Two coolers had been used for the single array system, based on miniature Peltier effect heat pumps (Figure 8) and larger ones (Figure 9). The larger pumps were more effective in cooling the array but would have suffered from three disadvantages in a six array system. These were:

i. They were bulky and required special insulation of their large cold surfaces to work efficiently.
ii. They consumed a considerable amount of stable DC power.
iii. They required a lot of water to cool them.

The design of the coolers based on the miniature Peltier heat pumps was re-examined. Redesign allowed the number of pumps to be doubled, from 2 to 4, and also increased their efficiency by improving the heat transfer from the array to the heat pumps. During trials it was found that this arrangement would cool the back of the array by 34°C below the temperature of the tap water supply (14°C in February) to -21°C and this was considered to be adequate. If the temperature should need further reduction, at some future date, the cooling water could be replaced by a cooling fluid supplied from a refrigeration type of chiller.

The four Peltier heat pumps for each array cooling system were electrically connected in series and drew 2 A at 6 V. Sufficient power supplies were available to supply the 12 A required.

The cooling water supplied to the hot side of the Peltiers had to remove 6.24 watts of pumped heat and 12 watts of I^2R heat from each array cooling system. These 18.24 watts are equivalent to 4.4 gm calories per second. This would require a water flow rate of at least 5 ml/s as efficient cooling requires that the water temperature rise be kept as low as possible (1°C). The constrictions within each cooling system would cause too much back pressure if all six coolers were connected in series with a water throughput of 30 ml/s. Consequently, the water supplied to the coolers had to be drawn in parallel off a manifold. All water hoses were cut to the same length in an attempt to equalize flow rates.

The dry nitrogen necessary to prevent fogging of the cooled array was fed to the six arrays through a manifold. Its pressure was controlled within the range of 8-15 cm of water head pressure.

7.2 Power Supplies

The power supplies for the 6 array control boards and for the Peltier coolers were distributed through sets of sockets fitted with irreversible plugs to maintain correct polarity. The general layout of the services within the direct reader light proof box is shown in Figure 46. Details of the power supplies are given in Appendix 7.

7.3 Location of the Plasma Power Unit

The RF generator for the ICP is cooled by a blower. Vibrations from the fan were picked up by the direct reader light proof box during the single array trial. The effect of the vibration on the stability of the system could be observed by watching the oscilloscope pattern of the array readout at short integration times. During an eight hour run of the system, the vibration was sufficient to move the spectral peak by one diode along the array.

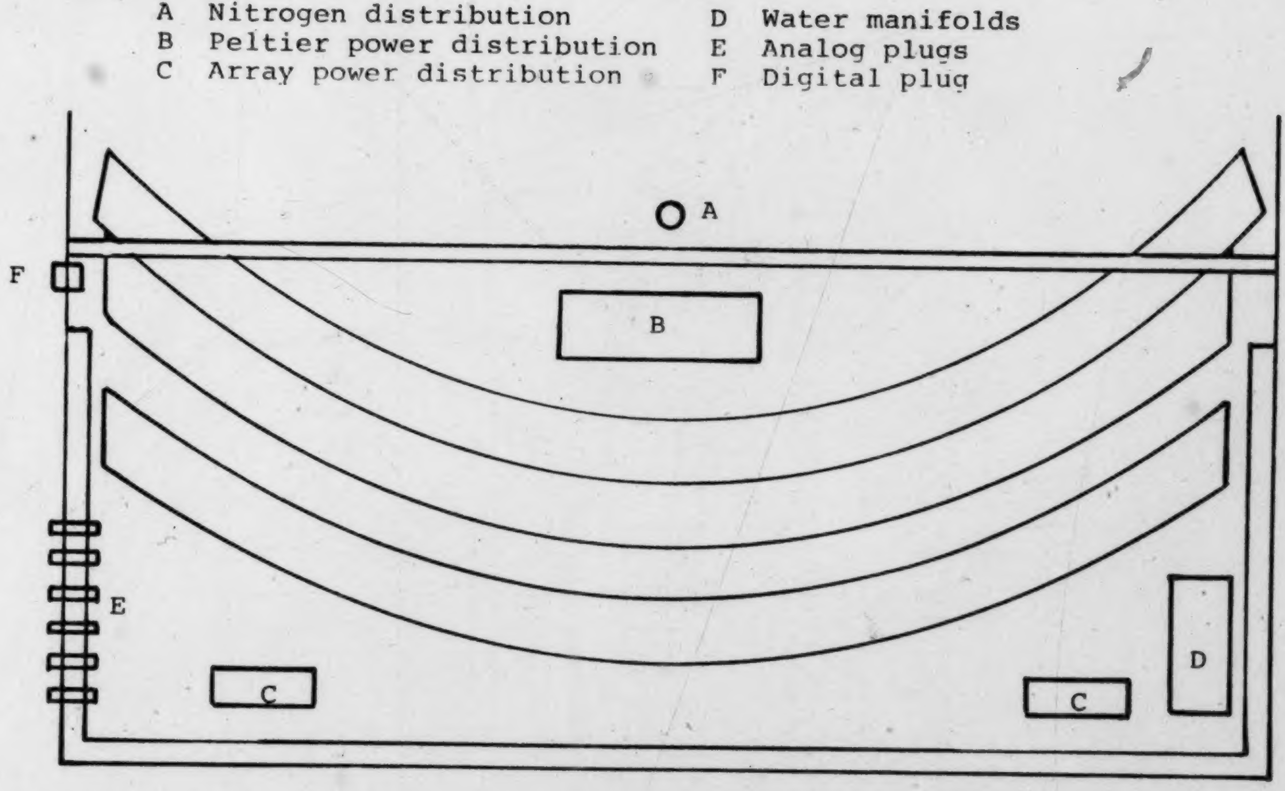

A Nitrogen distribution
B Peltier power distribution
C Array power distribution
D Water manifolds
E Analog plugs
F Digital plug
A
F
B
E
C
C
D

Figure 46. The layout of the services in the focal plane area of the six array system.

For the multi-array system, the power unit was moved out of the room, taking advantage of the 13 ft long cable connector between the power supply and the matching network at the plasma head. This effectively removed the vibration problem.

This completes the description of the design and construction of the multi-array direct reader. Its utility is described in Chapter VI.

CHAPTER VI

USE OF THE PHOTODIODE ARRAY DIRECT READER

The photodiode array direct reader has to be evaluated as a spectrometer.

The data presented in Chapter IV have shown that, when allowance is made for the instrumental effects caused by the diffraction grating, the photodiode array spectral windows have detection limits equivalent to those obtained with a photomultiplier tube system. This chapter describes how the spectral windows obtained with the diode array system can be applied to the problems associated with photomultiplier tube systems described in Chapter I. Where a background correction is applicable it is applied. Where this is not possible, due to gross interference, an approximate correction may be made. When corrections are not made, knowledge of the existence of an interference may prevent inadvertent release of incorrect analytical data.

Background corrections are usually calculated from data obtained from the array recording the analyte emission but, in the case of direct line overlap, they can also require calculations from data obtained from other arrays.

In order to demonstrate the versatility of the system, the direct reader is set up and used to solve an analytical problem.

1. Spectral Resolution

One of the criteria for evaluating a spectrometer is its ability to resolve two closely spaced lines. The photodiode arrays record spectral measurements at 0.014 nm intervals. A study was made of the resolution of pairs of lines of approximately equal intensity by recording the spectra of doublets.

The diode array will not resolve Li I 670.776 nm from Li I 670.791 nm as these lines fall on adjacent diodes. It will resolve Na I 330.237 nm from Na I 330.298 nm where the peaks are 4 to 5 diodes apart. It will resolve B I 249.773 nm from B I 249.678 nm where the peaks are 7 diodes apart. It will resolve Na I 588.950 nm from Ar I 588.858 nm sufficiently for a corrected value to be obtained at the ppm level.

It has shown a dip between Fe II 263.132 nm and Fe II 263.105 nm, two lines of equal intensity 2 diodes apart. However this took careful adjustment of the position of the diode array. Differences in wavelength of this order (.027 nm) which have only a single diode separating the peak diodes would not be resolved with normal direct reader usage.

Some examples of resolution are shown in Figure 47.

In general usage, the photodiode arrays show separation (but not to the base line) of two peaks of similar intensity if they are 4 diodes apart (.06 nm) and for two peaks with a considerable difference in intensity if they are 7 diodes apart (.1 nm). This may be enough to allow for peak height correction unless one of the peaks shows considerable pressure broadening or is a strong enough emission to saturate the photodiodes.

The resolution of a pair of spectral lines is dependent on their individual line widths. This in turn depends on several factors including the source, the entrance slit, the diffraction grating and the spacing intervals permitted for the detectors.

Within the spectral source the line width is controlled by several effects [12]. The natural line width at half intensity arising from the application of the Heisenberg uncertainty principle is generally of the order of 12 fm, which is insignificant. Doppler broadening leads to half intensity line widths of the order of .02 nm to .001 nm. Collision or pressure broadening is much more important, particularly when strong Stark effect occurs as it does with certain ion lines. The line width at half intensity is widened to about .03 nm for Ca II 393.366 nm but the major effect is on the spread of the

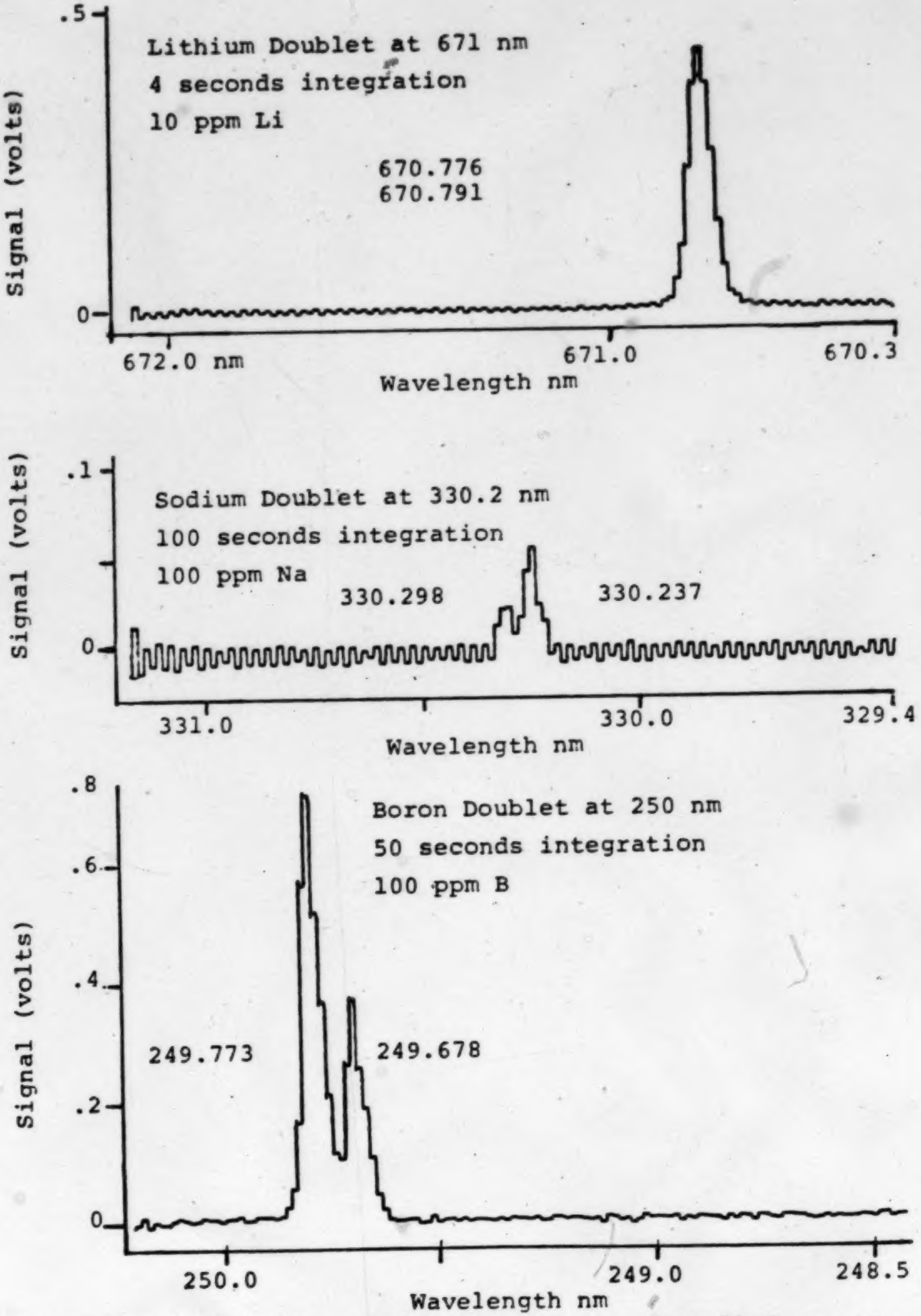


Figure 47. Spectral resolution with the photodiode array.

wings of the line which extend over more than 1 nm.

The fixed width of the entrance slit sets a minimum image width of the line at the focal plane of the instrument of 25 μm, equivalent to a spectral width of 0.014 nm.

Rayleigh's criterion for the resolution of two spectral lines is that one line be separated from the other by at least half of the distance between the first minima of the sinc^2 function of the line. This depends on the number of lines ruled on the diffraction grating and for first order spectra is given by

$$\frac{\lambda}{\Delta\lambda} = \text{total number of lines}$$

The direct reader grating is 63 mm wide with 1,180 lines per mm to give a total of 74,000 lines. The value of $\Delta\lambda$ (resolvable line interval) lies between .0027 nm at 200 nm and .0103 nm at 760 nm.

The diffraction grating may cause additional line broadening due to astigmatism.

The photodiodes on the array are spaced at 25 μm intervals. Actually each photodiode records all of the light falling on a 13 μm width and part of the light falling on a 12 μm width on either side (Figure 3). It will thus show some response to light over a spectral range of .02 nm. Thus the diode interval and the entrance slit width are the limiting factors governing the resolution except for cases of strong collision broadening or astigmatism.

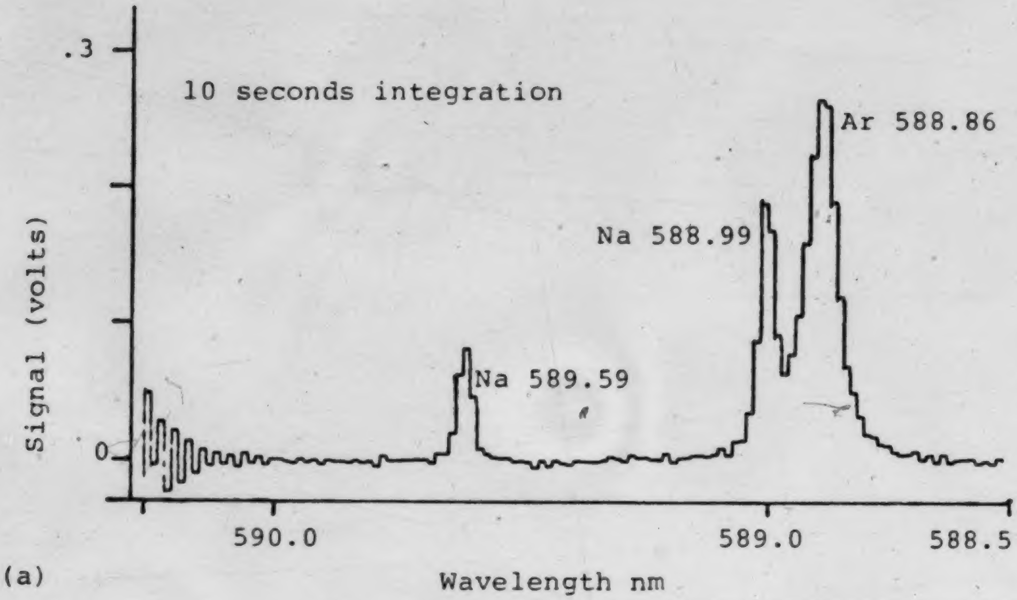
The 25 μm diode interval is approximately correct for the direct reader system. If it were much smaller, the entrance slit would have to be reduced to obtain better resolution. The Doppler effect might also come into play especially for the lower atomic weight elements excited in the hottest part of the plasma.

2. Wing Overlap

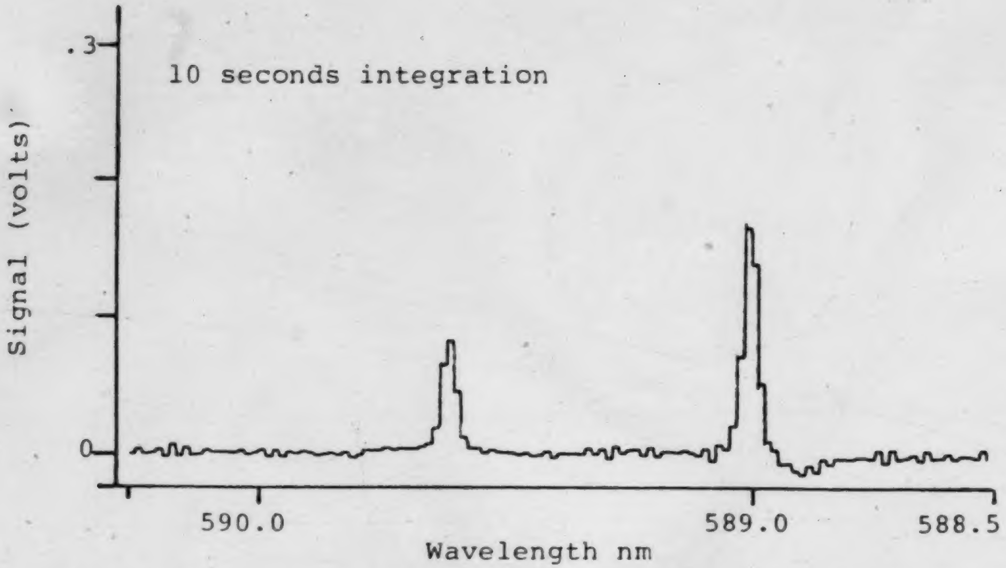
Spectral line overlaps restrict the use of some emission lines for analytical purposes with a photomultiplier tube system. This can be a major problem with an analytical sample containing many different elements. In some cases the most strongly emitted line cannot be used and the weaker lines chosen reduce the sensitivity at low concentrations. Wing overlap occurs when the peak height of an analyte line is increased by some portion of the emission of a nearby concomitant or carrier line. This is particularly important with the inductively coupled plasma source as collision effects can spread the wings of a line over 1 or 2 nm. Wing overlap may also involve argon lines which tend to be variable in intensity. Argon lines are not a problem below 300 nm wavelength but have to be considered when such low wavelength ultraviolet lines are used in second order [51].

The diode array output for a 15 ppm solution of sodium is shown in Figure 48(a). The Ar I line at 588.86 nm is stronger and broader than the Na I line at 588.99 nm and causes considerable wing overlap. Because of this, the weaker 589.59 nm line is generally used in direct readers. The value of the argon line could be cancelled by subtracting the spectrum of water (to give Figure 48(b)) but this would require a separate analytical run and would still have the chance of error due to variation in the argon emission. The diode array allows an alternative method.

The argon line is broad and symmetrical. Although its intensity may vary, its position does not. It has been established that a good value for the emission due to argon at the wavelength corresponding to the sodium line can be obtained from a measurement on the opposite side of the argon line. Thus in Figure 48 the sodium line peak is at diode number 90. The argon emission at this diode is the same as that at diode 105, within the noise limits of the array. The sodium line is relatively narrow and at such low concentrations does not have any significant effect on the signal received by the array 15 diodes away



(a)



(b) Water spectrum subtracted

Figure 48. The 589 nm doublet for sodium (15 ppm Na).

from its peak. The two subtraction methods are compared in Table 20 for five different samples with a sodium concentration range of from 4 to 20 ppm.

The effect of a high concentration of calcium on the aluminum line at 396.2 nm is shown in Figure 49. The curved baseline is due to the line falling on the extended wing of calcium II 396.8 nm. The aluminum line is also affected by wing overlap from the line, also due to calcium, next to it at 396.0 nm.

Sufficient of the curved baseline is present to allow the use of a curve fitting computer program developed by Warme [52]. This program is used to estimate the position of the baseline beneath the aluminum line. The program uses a least squares fit to select a polynomial equation for the curve. It has to be used cautiously as it tends to attach too much significance to the irregular variations in the curve. It may be possible to develop a more suitable program based on the expected profile of the broadened line. Larson and Fassel [12] refer to the Voigt profile which is a combination of Gaussian shape due to Doppler broadening, and Lorentzian line shape due to collision broadening.

The estimated background level did not completely correct for the calcium presence. The corrected values for aluminum were up to 20% high for aluminum

Table 20. Comparison of two subtraction methods for the removal of the argon interference on the sodium 589.0 nm line.

Peak Height in Volts Normalized To 1 Second Integration	
Water Spectrum Subtracted	Wing Value Subtracted
.01416	.01438
.01821	.01809
.01814	.01822
.00537	.00555
.00511	.00556

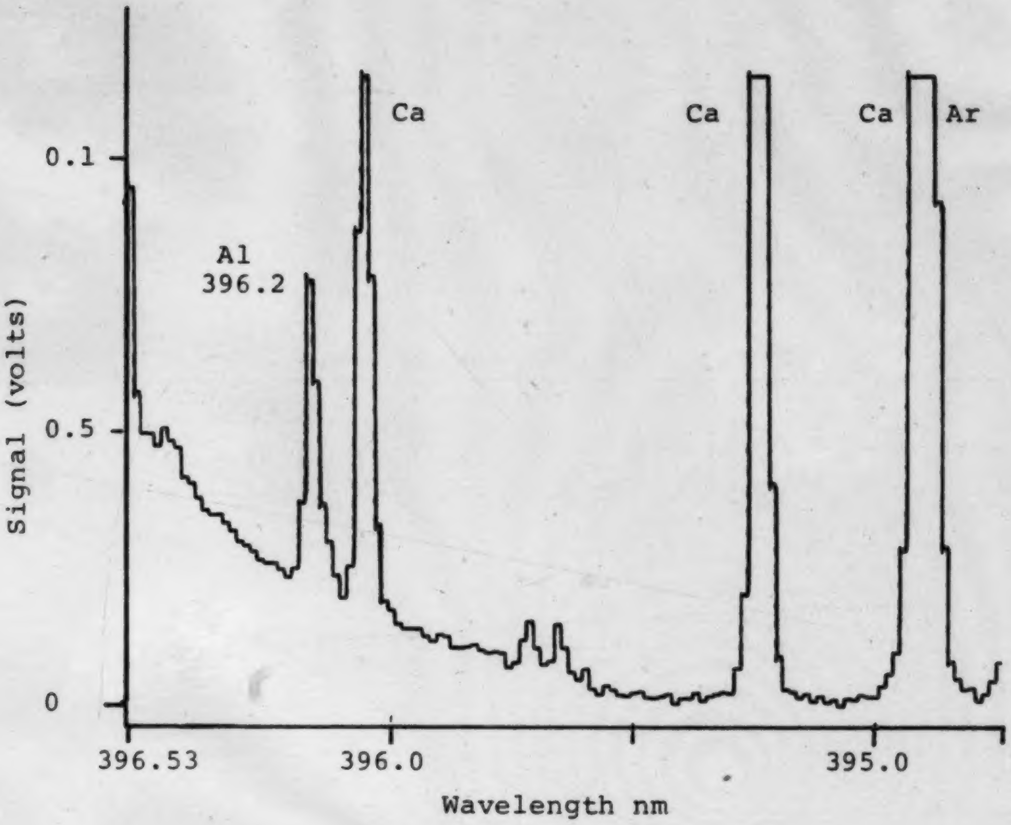


Figure 49. Interference by 100 ppm calcium on the aluminum line at 396.2 nm (2.5 ppm Al).

concentrations in the 2.5 to 10 ppm range. Some of this would be due to the wing overlap of the adjacent calcium line.

The collision broadened wings of the calcium line extend at least 2 nm from the line centre. Calcium, like the other alkaline earth elements, is highly ionized in the ICP and the ions undergo $^2S_{1/2}$ - $^2P_{3/2,1/2}$ transitions to give spectral doublets corresponding to those given by the alkali metal neutral atoms. The emitting species is positively charged and exists in an atmosphere rich in free electrons. The ions are thus exposed to intense but variable electric fields. These fields cause perturbations in the energy levels of the single outer electron of the ion due to the application of the linear Stark effect. These energy level changes force variations in the spectral transitions and lead to line broadening.

3. Direct Spectral Overlap

Direct overlap occurs when two spectral lines are close enough together so that their peaks cannot be resolved. This is a major problem with direct readers as very minor spectral lines of a concomitant element can cause significant spectral interference if the concomitant concentration is much higher than that of the analyte.

The only solution is to calculate the signal due to the concomitant by measurement of its concentration with another spectral line. The apparent analyte concentration due to the concomitant is then subtracted from the measured analyte signal. Not all spectral overlaps are obvious and for those overlaps for which corrections are applied there is a deterioration of precision for the analyte due to the addition of the further uncertainty associated with each concomitant.

A direct overlap occurs when traces of zinc are determined in the presence of high concentrations of copper or nickel. The zinc line at 213.86 nm is overlapped by the minor copper line at 213.85 nm or the nickel line at 213.86 nm.

The direct reader was set up with three photodiode arrays covering the zinc 213.86 nm line second order at 427.71 nm, the copper line at 324.75 nm and the nickel line at 352.45 nm. There was a fortunate coincidence of a weak copper line at 427.51 which was recorded by the same array as the zinc line. The test solutions were 10 ppm zinc with 1500 ppm of copper or nickel. Solutions of copper and nickel (2000 ppm) were used as standards for calibration. The copper interference is illustrated in Figure 50. The minor spectral feature of copper causes significant interference when present in a much higher concentration than the zinc analyte.

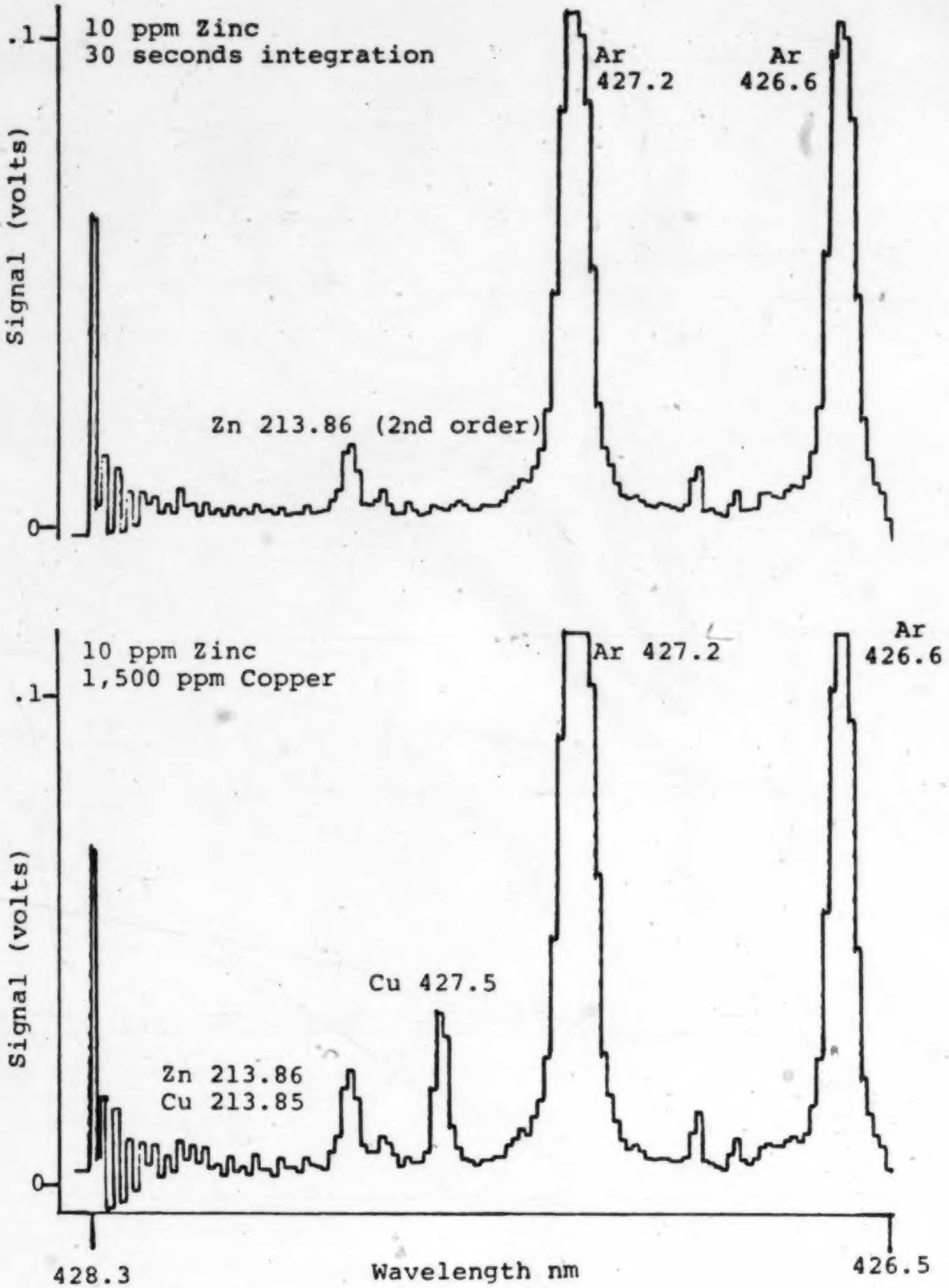


Figure 50. Direct overlap of copper on zinc.

The corrective process is illustrated by Table 21. The correction calculated was a little low for the copper concomitant and too high for the nickel. The nickel correction error appears high until one considers that it involves a total measurement error of less than 4 mV. The standard deviation of the background against which the zinc signals are measured is of the order of 1.5 to 3 mV and the calculation involved the use of four sets of measurements (2 of the standard nickel line and 2 of the zinc line) and then comparison with a fifth.

The errors illustrate the difficulty associated with direct overlaps. Other workers have reached similar conclusions. Foster, Anderson and Parsons [51], following a basic study with a scanning echelle monochromator, state, "Direct spectral overlaps are not totally correctable and cause deterioration of detection limits and nonlinearity of analytical curves."

4. Recombination Continua

The recombination of the singly charged ions of calcium, magnesium and aluminum with electrons in the plasma is known to raise the background level for spectral measurements at wavelengths below 302 nm. The effect on the background level was investigated by including 500 ppm of calcium, magnesium and aluminum (separately) into test

Table 21. Correction for direct overlap. (See Figure 50.)

Concomitant and Wavelength Used to Estimate	Signal Values in Volts Normalized to 1 Second Integration Time					
			Test Solutions			
	Value of Signal of Standard A	Value of Signal of Standard at Zinc Line Position B	Signal Value for Cu or Ni C	Signal As Zinc D	Estimated Zinc Signal $D - \frac{C.B}{A}$	10 ppm Zinc Signal for Comparison (Taken on Same Settings)
Copper 324.75 nm	2.82	3.19×10^{-4}	2.20	6.95×10^{-4}	4.46×10^{-4}	4.06×10^{-4}
Copper 427.51 nm	1.43×10^{-3}	3.19×10^{-4}	1.03×10^{-3}	6.95×10^{-4}	4.65×10^{-4}	
Nickel 352.45 nm	.859	3.30×10^{-4}	.626	9.20×10^{-4}	6.80×10^{-4}	8.07×10^{-4}

solutions containing 100 ppm of zinc and cadmium. The background was measured for the Cd I line at 214.4 nm and the Zn I line at 213.9 nm in both first and second order. No significant changes were noted in the diode to diode variation or in the background level.

Another wing overlap was noted between calcium I 428.936 nm in first order and cadmium 214.441 nm in second order at 428.882, illustrating again the advantage of having a spectral window (Figure 51). If the recombination continua had significantly raised the baseline, the use of off-peak diode measurements to calculate the background would have automatically corrected for it.

5. Stray Light Due to Grating Defects

There are three relatively strong emission lines in Figure 49, all due to calcium. They are at 396.0 nm, 395.2 nm and 394.9 nm. Not one of these lines appears in any published table of atomic emission lines. They are all Rowland ghosts caused by periodic inaccuracies of the machine that ruled the master diffraction grating. They are relatively intense because their parent lines are extremely strong emissions. The line on the right appears broader than its neighbour because it has a stronger parent and also because it cannot be resolved from the adjacent argon line at 394.9 nm.

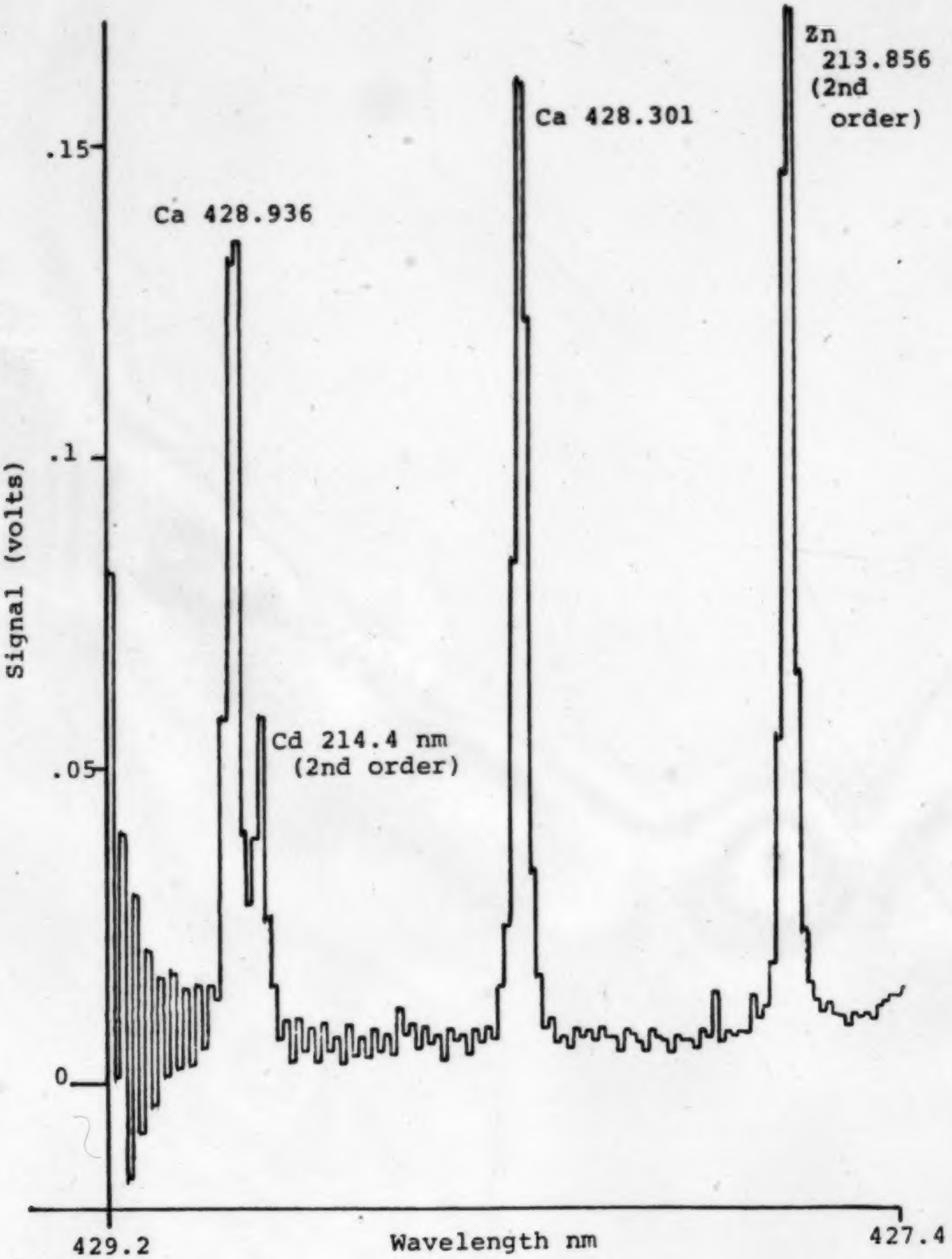


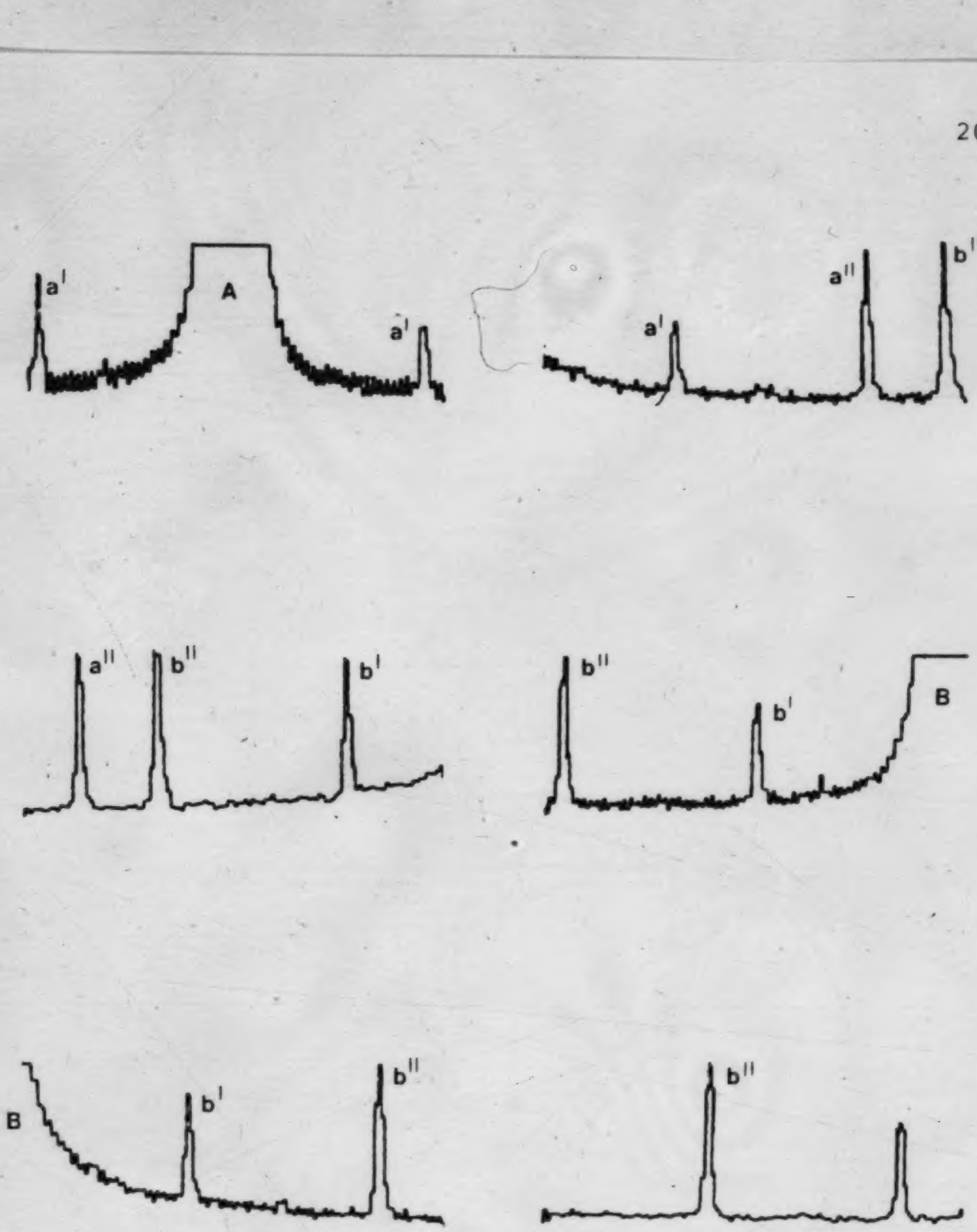
Figure 51. Wing overlap of calcium (50 ppm) on cadmium (100 ppm). 10 seconds integration.

By use of separate measurements, the peak height of these ghosts was compared to that of the calcium II line at 396.8 nm. Reading from left to right in Figure 49, the peak heights of the calcium ghosts compared to the 396.8 nm parent are .0032, .0075 and .0077. The first line is the first order ghost from the 396.8 nm parent, the second line is the second order ghost from the same parent and the third line is the second order ghost from the parent Ca II line at 393.4 nm.

The diode array window is not wide enough to show the whole symmetrical pattern of the ghosts. By moving the array along the focal plane of the direct reader, the whole pattern can be found. This is illustrated in Figure 52 which also shows how the broad wings of the parent lines can dominate the background for any other elemental lines in this region of the spectrum.

More modern gratings ruled with interferometric control are claimed to have first order ghost to parent intensity ratios of .00001 [10]. Holographic gratings are now being offered that are ghost free.

The ghost intensities illustrated by Figures 49 and 52 seem excessive in comparison to those seen with a modern monochromator. However it must be considered that the direct reader was obtained as a working instrument from an industrial installation with the grating quality probably typical of those made at the time.



A 396.8 nm parent line (array saturated)

a' 396.8 nm first order ghost

a'' 396.8 nm second order ghost

B 393.4 nm parent line (array saturated)

b' 393.4 nm first order ghost

b'' 393.4 nm second order ghost

Figure 52. The Rowland ghosts associated with CaII 396.8 and CaII 393.4 nm.

The grating defects characterize the ruling engine used to make the master grating.

The spacing of the ghosts is given by [11]

$$\lambda' = \lambda\left(1 + \frac{m'}{mn}\right)$$

where λ is the wavelength of the parent line, λ' is the wavelength of the ghost of order m', m is the spectral order of the parent line and n is the number of lines ruled per turn of the lead screw of the ruling engine. For example, an engine ruling 500 lines for each full turn of the lead screw would expect to have ghosts at intervals of .79 nm in the spectral region of these lines and this approximates the spacing observed.

The relative intensity of a ghost is given by [53]

$$\frac{\pi^2 m^2 e^2}{a^2}$$

where m is the order of the ghost, e is the displacement of the periodic error, and a is the correct grating line interval.

If the first ghost is taken as first order, the displacement can be calculated as 1.8%, which for an engine ruling 1,180 lines per mm corresponds to a 15 nm error in the accuracy of the lead screw.

Returning to the problem of interference with the aluminum line, there is an alternative aluminum line at 394.4 nm. This is only 60% as intense as the line at 396.2 nm but for this grating and for a matrix high in calcium, it is the better choice because it lies further from the first order ghost, in this case, of the calcium 393.4 nm line. Thus the spectral window provided by the photodiode array supplies the necessary information to select lines to suit the matrix as well as the means to allow such a choice.

6. Interference from Molecular Bands

All of the spectra considered so far have been due to electronic transitions within an atom. However certain molecular species can also exist in the plasma and these undergo vibrational and rotational transitions as well as electronic ones. Just as the rotational transitions add fine structure to vibrational spectra in the infra-red region, so the rotational and vibrational transitions add fine structure to the electronic spectra in the visible and ultraviolet region where they cause spectral interferences.

The main molecular species that can occur in atomic spectroscopy are CN, NO, NH and OH. With the inductively coupled plasma source CN bands are not a problem if organic compounds are avoided. If the flow rate of the plasma (coolant) gas is high enough, the NO and NH spectra are not a problem. However the OH bands are always present when aqueous solutions of analyte are used.

6.1 Problems Caused by Hydroxyl Bands

Dieke and Crosswhite [54], working with an oxy-acetylene flame source and a 21 ft radius diffraction grating, identified hydroxyl lines over the range 281.1 nm to 354.6 nm. Many of these lines are of low intensity and so do not cause interference but some are intense enough to cause serious problems. According to Foster, Anderson and Parsons [51], the ICP background contains 116 major hydroxyl features between 281.0 nm and 294.5 nm and a further 180 between 306.0 nm and 324.5 nm.

As a typical example of the interference caused by hydroxyl, consider Figure 53 which shows the aluminum lines at 309.3 nm and 308.2 nm for a 10 ppm solution and 10 second integration time. The aluminum I 309.3 doublet (unresolved) and the aluminum I 308.2 line are obvious but the background shows other spectral features as well as the odd-even pattern of the array. It is not clear which values of background could be used to correct the aluminum values.

In order to characterize the background, the array was retuned to minimize odd-even pattern and the spectrum

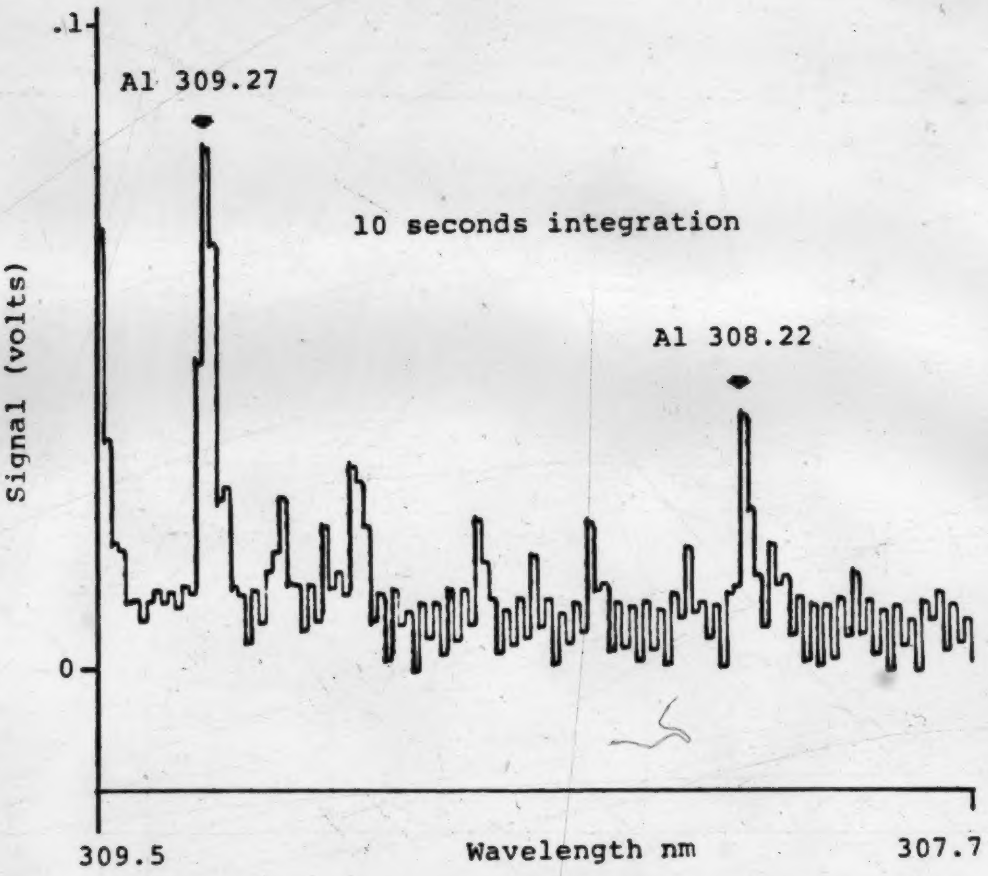


Figure 53. The aluminum lines at 309.3 nm and 308.2 nm showing hydroxyl bands. 10 ppm Al.

due to aspirated water obtained. This is shown with the signal axis extended in Figure 54. All of the peaks are due to hydroxyl and can be assigned to transitions using the tables published by Dieke [54]. The aluminum I doublet at 309.271 and 309.284 nm is augumented by the hydroxyl peak at 309.279 nm with another more intense hydroxyl peak close by at 309.239 nm. The aluminum I line at 308.215 nm lies in a trough between the major hydroxyl peaks but has a minor peak at 308.207 nm on the next diode which, combined with the effects of major peaks at 308.167, 308.162 and 308.154, raises its background level.

Corrections would be required for both the 309.3 and 308.2 nm aluminum lines. There are two possible ways to correct for the hydroxyl interference. One is by direct subtraction of the water signal and depends for its precision on the water signal being constant. The other method is by estimating the contribution of the hydroxyl emission from another hydroxyl peak on the same array but away from the aluminum lines. Neither method is really satisfactory. The water subtraction is shown in Figure 55. The peak height for aluminum at 309.3 nm after subtraction of water background was .03973 V with a background standard deviation of .00232 V (4 points). However the standard deviation of the water background calculated from 4 runs was .00725 V. Thus the variability

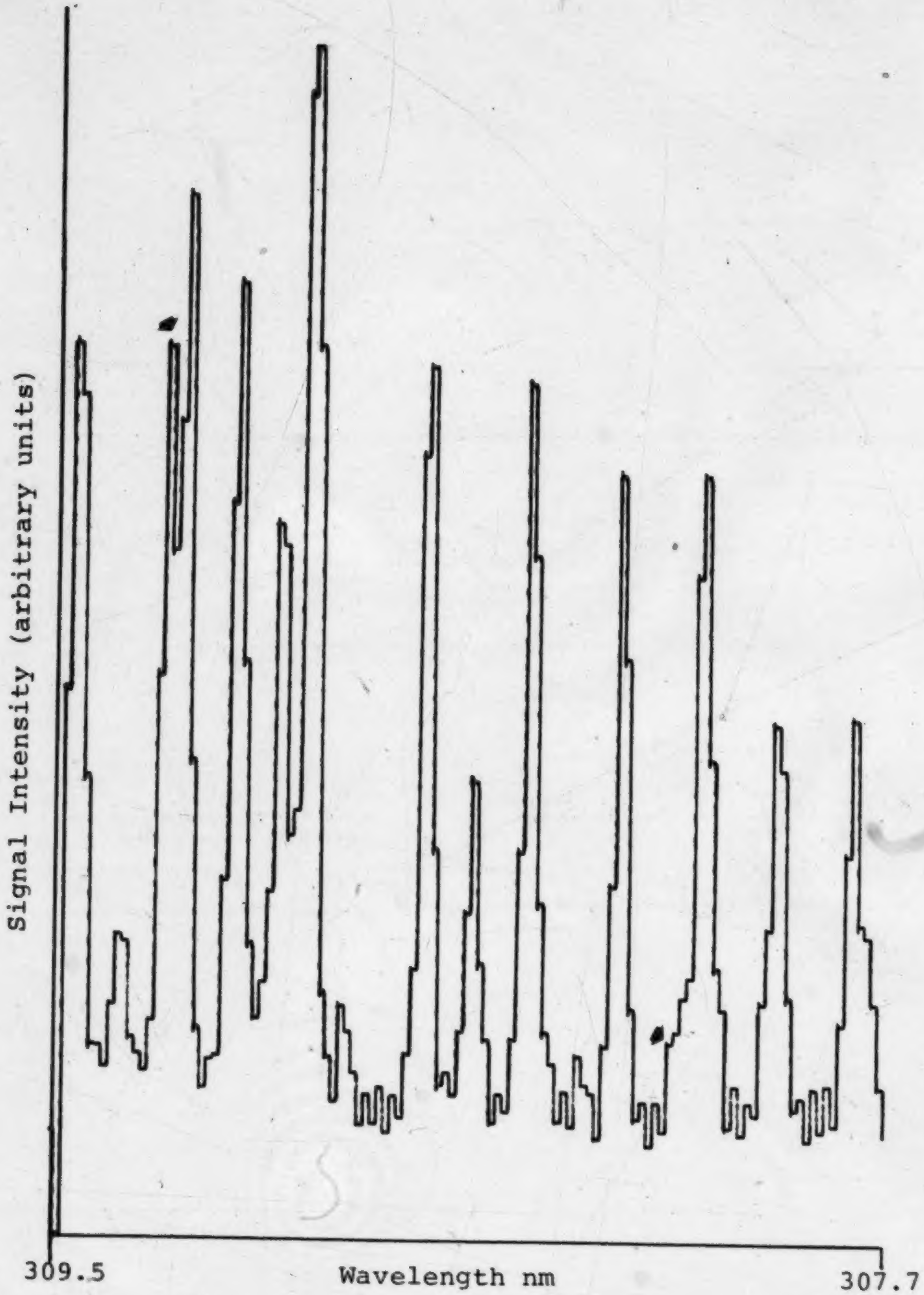


Figure 54. The hydroxyl pattern for water in the 308 nm to 309 nm range. (The arrows indicate where the aluminum lines would be.)

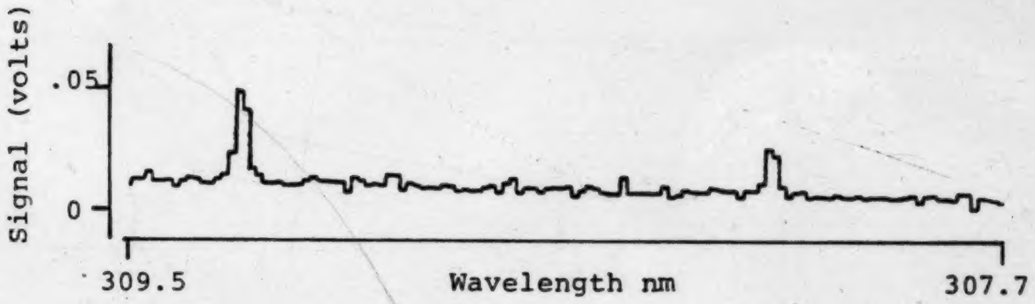


Figure 55. The aluminum lines at 309.3 nm and 308.2 nm after water background subtraction. 10 seconds integration. 10 ppm Al.

of the signal due to the hydroxyl background reduced the signal to noise ratio of the analyte line from 17 to 5.5.

Aluminum has its three most sensitive lines subject to spectral interferences. This has led to the use of the doublet at 237.3 nm for aluminum in photomultiplier tube based direct readers. In order to ease the crowding of the focal plane array of a direct reader in the ultraviolet region, this emission may be viewed second order where it is within .05 nm of a weak argon line at 474.7 nm [51]. This type of close proximity of spectral lines to potential interferences forces the instrument manufacturer to use narrow exit slits and to go to considerable trouble to maintain constant optical positions for the exit slits. This may involve thermostatic control of the whole direct reader dark box and the maintenance of a constant atmosphere within it.

The hydroxyl spectra are much weaker in the region of the copper I line at 327.4 nm. Integration times of ten times those used for the aluminum area were required before they became significant (100 seconds versus 10 seconds). They are illustrated in Figure 56. Again Dieke's tables [54] allow the peaks to be assigned to transitions.

The 327.396 nm copper line is close to a hydroxyl line at 327.421 nm. The alternative copper line in the

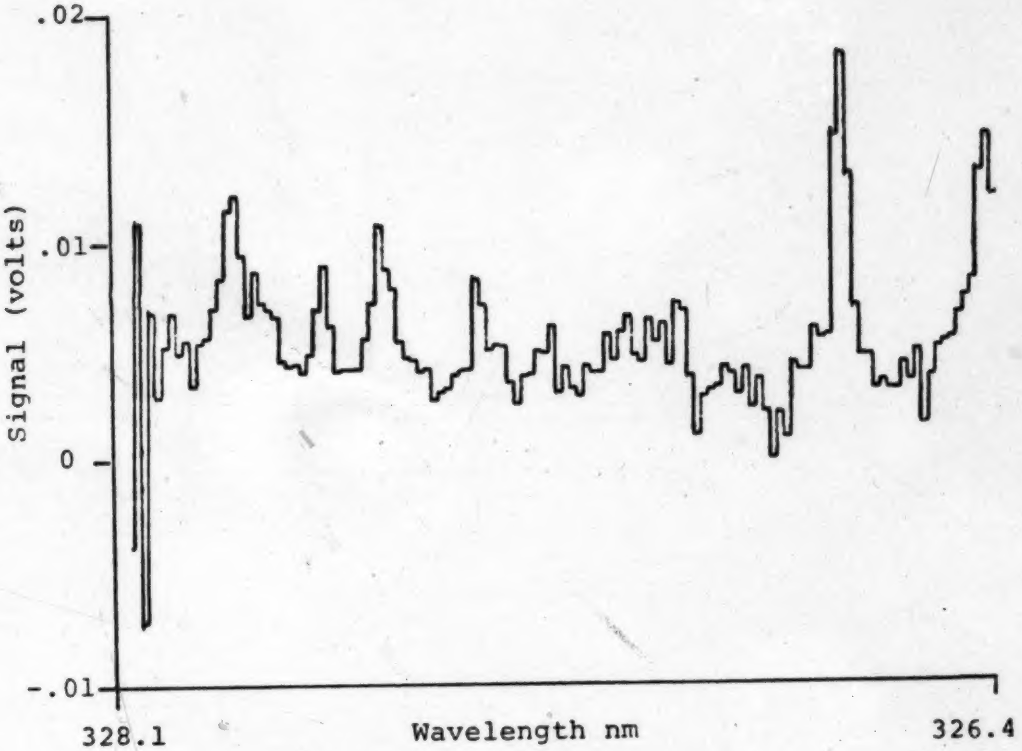


Figure 56. The hydroxyl pattern in the 327 nm to 328 nm region for 100 seconds integration.

same region at 324.754 nm is close to the hydroxyl lines at 324.736 nm and 324.762 nm. However the intensities of the hydroxyl lines, as measured by Dieke, are about one fiftieth of those in the aluminum region and this reduces their effect on the detection limits of the analytes.

6.2 Problems Caused by Nitric Oxide Bands

The cadmium II line at 214.4 nm is in the same spectral region as a NO band head if the molecular bands are present. The spectrum recorded for 50 s integration time of a 1 ppm cadmium solution is shown in Figure 57. The cadmium 214.4 nm line is shown in second order at 428.9 nm. The black arrows indicate single diode anomalies that become significant at long integration times. The features marked b and the general increase in background towards the lower wavelengths are present in the spectrum of water and may be due to molecular spectra or to stray light.

Because the spectrum is second order, direct assignments are difficult to make. The γ system of NO bands, that has been observed for the ICP at low plasma gas flow rates, has a band head at 214.91 nm (429.82 nm in second order) [55], just to the left of the array. Application of a pair averaging technique to reduce the effect of the odd-even pattern to the left of the array indicated only a slight rise in the background towards

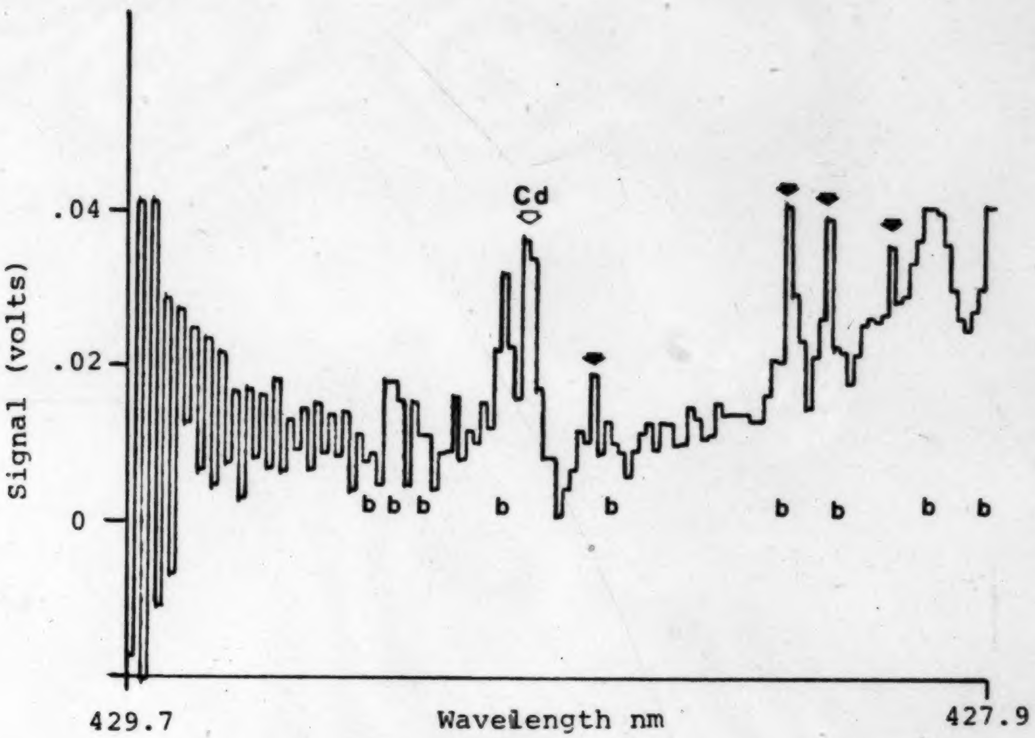


Figure 57. Background patterns near the Cadmium II 214.4 nm line (second order). 50 seconds integration.

longer wavelengths, not as large an effect as that to the right, lower wavelength end, of the array. Although no direct assignments could be made, there are enough background features to complicate the read out of the cadmium signal.

7. Use of the Direct Reader for Analysis

One of the advantages that the photodiode array has over the exit slit-photomultiplier tube combination is the ease of location of spectral lines. This allows the diode arrays to be moved along the focal plane of the direct reader to suit the analytical problem. Because the detectors are easily moved, the number of detectors can be reduced. Banks of 40 to 60 exit slits each with its own detector are no longer necessary. The diode arrays can be placed to detect the elements of interest in a particular analyte matrix. Where direct overlaps occur, the overlapping elements also need to be determined. A single array can be used to measure several elements provided that spectral lines are chosen to suit the concentration ranges of the various analytes. A single array can be used to record spectral emissions of different spectral orders. Examples of this have been illustrated in Figures 50 and 51.

To demonstrate the flexibility of the photodiode array direct reader it was set up to measure the main metallic elements in several commercial bottled waters. Three bottled waters from three different sources were obtained. To add variety a locally produced beer, a local well water and the municipal supply were also analyzed.

The elements determined were calcium, iron, magnesium, manganese, sodium and strontium. Potassium is also usually present in water samples but the potassium I 404 nm doublet is too weak an emission for analysis of ppm level concentrations. The much stronger emission at 766 nm is just outside the normal geometric range of the direct reader (it could be brought into range if a shorter array carriage could be made). Zinc is also of interest but it could not be obtained simultaneously with the other elements because of the limited window of the diode arrays compared with the width of the array carriage.

The Apple II+ computer was booted using the disk ARRAY SELECT. The program ARRAYSET was loaded and the spectral text files for the 7 elements (including zinc) entered. This gave an initial ordered list of 141 spectral features each showing its spectral position, element, species code (atom or ion line), wavelength, relative detection limit (ppb from Winge's table [43]) and spectral order.

Most of these features were ruled out as analytical lines by considering the instrumental limitations of the direct reader combined with some knowledge of the concentration ranges to be expected. The remainder were carefully examined and eventually four spectral windows were chosen to cover the following spectral features:-

Array 0

Mn	I	260.6 nm
Fe	II	259.9 nm
Fe	II	259.8 nm
Fe	I	260.7 nm

Array 1

Mg	II	293.7 nm
Mn	II	293.3 nm
Mn	II	293.9 nm

Array 2

Ca	I	422.7 nm
Sr	II	421.6 nm

d. Array 3

Na	I	589.0 nm
Na	I	589.6 nm

The array carriage positions were calculated using the program LINELOC and finally placed along the focal plane of the direct reader using the signals from 1000 ppm solutions of the various elements.

The time taken for the set up operation was approximately 2 hours. Planning the layout took slightly more than an hour. Moving the array carriages and the RC1024S boards, tuning the arrays and locating the lines took 50 minutes for all four arrays.

Solution standards were prepared at high and low concentrations for the elements of interest. The concentrations were selected to straddle the expected ranges of the elements in the samples. The samples were analyzed with the integration times for the various arrays selected to bring the signal values within the dynamic range of the arrays. Data values were extracted from the array signals and concentrations calculated by linear interpolation of the values for the solution standard.

The iron II line at 259.9 nm was subject to background pattern and gave signals with considerable variability so it was not selected as an analyte line.

The results are given in Table 22 and compared to values quoted on the bottle labels and to a previous sampling of the local waters analyzed last year with a photomultiplier tube based direct reader.

The precision (relative standard deviation) of the measurements of the calibration standards were in the 1 to 3% range for calcium, magnesium, sodium and the higher level of strontium. The precisions of the analyte runs for the major elements varied from less than 1% to 12% with one exception (magnesium in municipal water had a relative standard deviation of 30%).

For manganese the relative standard deviation was 10 to 18% while for iron it was 17 to 35%. The low

Table 22. Analytical resuts for water samples.

SAMPLE IDENTITY	VALUES IN PARTS PER MILLION							
	Ca 422.7	Mg 293.7	Sr 421.6	Na 589.6	Na 589.0	Mn 260.6	Fe 260.7	Fe 259.8
Perrier Water	172	*	0.59	15	14.0	*	*	*
Apollinaris Water	111	120	0.14	563	568	*	*	*
Mont Blanc Water	106	16	0.16	6		*	*	*
Beer (Red Deer)	55	120	0.27	53	51	0.22	1.8	2.1
Well Water	92	12	0.9	62	56	0.44	4.7	4.6
Municipal Water	70	9	0.33	2	3	*	*	*
	TYPICAL VALUES FROM BOTTLE LABELS							
Perrier Water	140	3.5	--	14	14	--	--	--
Apollinaris Water	95	126	0.17	572	572	0.03	0.02	0.02
	VALUES FROM PREVIOUS SAMPLINGS [56]							
Well Water	68	15	0.65	65	65	0.37	3.7	3.7
Municipal Water	40	6	0.26	20	20	--	--	--

*Below detection limits of 0.02 ppm for Mn and 0.2 ppm for Fe.

concentrations of manganese and iron necessitated the use of long integration times with consequent build up of background irregularities.

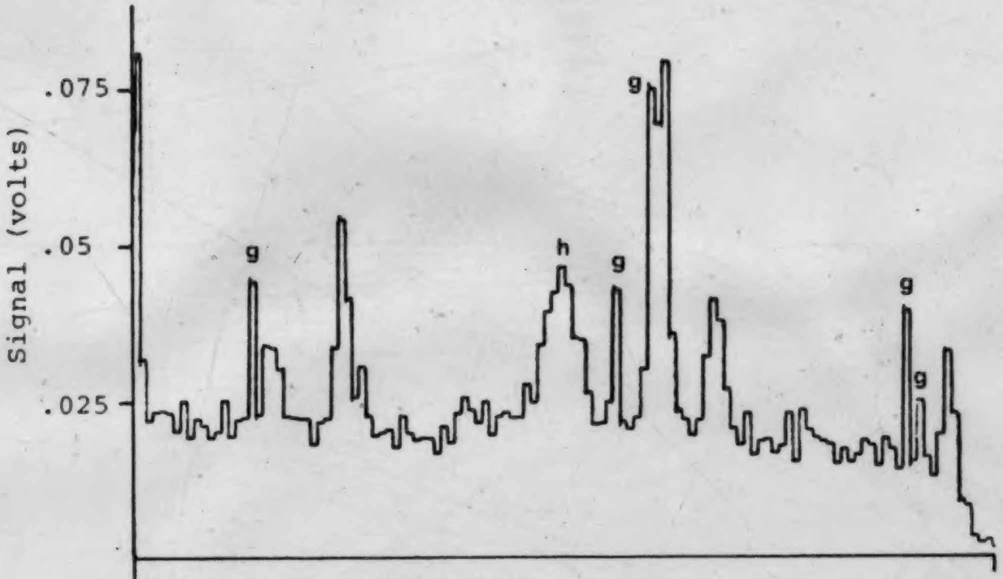
8. Background Subtraction and Other Correction Methods

The photodiode array output displayed on the video monitor allows direct inspection of the background against which the emission signal must be measured. With the exception of direct overlaps, all interfering spectral features become obvious. Because both the analyte line and the background are recorded by the data logging system, and if required saved to disk, the correction method can be selected and applied later.

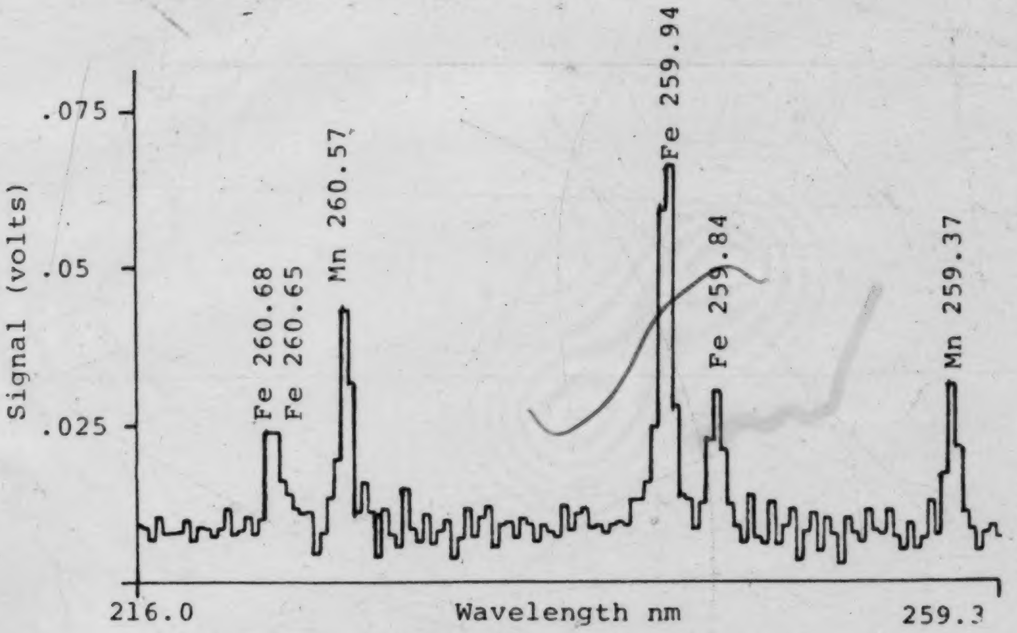
Background corrections can involve the complete subtraction of a measured background spectrum or the calculation of a baseline value from off-peak diodes of the same analytical run or both. If the background level is reproducible between data measurements, a simple background subtraction is sufficient. However, especially with measurements involving long integration times for low analyte concentrations, it is usually followed by use of an off-peak background correction factor.

Background subtraction is useful for removing or reducing the interference generated in the source other than by the elements of the analyte matrix. If they are sufficiently constant, interferences from argon and OH can be removed by subtracting the spectrum of aspirated water. The same subtraction will also remove the odd-even pattern, glitches and dark current variations of the photodiode array which can give false readings, especially at long integration times. These same array generated problems can also be removed by subtracting the signals generated by the diode array held in the dark for the same integration time. The argon line at 588.9 nm interferes with the sodium line at 589.0 nm as shown in Figure 48(a). Subtraction of a water background spectrum gives the corrected sodium line as shown in Figure 48(b). At the same time it cleans up the odd-even pattern to the left of the spectrum. The efficacy of this method for removing molecular band interference can also be observed by comparing Figures 53 and 55.

The spectrum shown in Figure 58(a) is that obtained for a 50 second integration time measuring the manganese and iron content of water from a local well. The interference consists mainly of single diode glitches (g) and a dark current anomaly (h). The cleaned up spectrum obtained by a water background subtraction is shown in 58(b). The background is still far from smooth and a background correction factor has to be calculated from off-peak diodes.



(a) Spectrum of well water



(b) Spectrum of well water with water background subtracted.

Figure 58. The manganese and iron spectrum of well water showing subtraction of array artifacts.

If concomitants in the analyte sample cause interference, then background subtraction will not suffice although it may be used to reduce odd-even pattern as a preliminary step. For concomitant interference, corrections must be obtained from the same analytical run. If direct overlap occurs the correction involves measurement of the concomitant elsewhere on the same or another array and prior calibration of the overlapping signal. For wing overlap, the same process can be used but may not be necessary. It may be possible to predict the corrected baseline value beneath the analyte line by estimating the contribution to the total diode signal from the interfering concomitant.

All calculations or projections involving an interfering signal increase the detection limits by reducing the precision. The diode array allows the operator to obtain prior knowledge of the symmetry of the interference imposed by the concomitant and this can be used to correct from the analyte run data. A complete printout of the diode values during the evaluation of the interference assists in this process.

The extraction of the analyte peak height has been incorporated as a system program. One of the options available in this program allows the operator to identify the diodes to be used in calculating the background level in much the same manner that the interpreter of a spectrograph photograph can select the positions for measuring the background intensity with a densitometer.

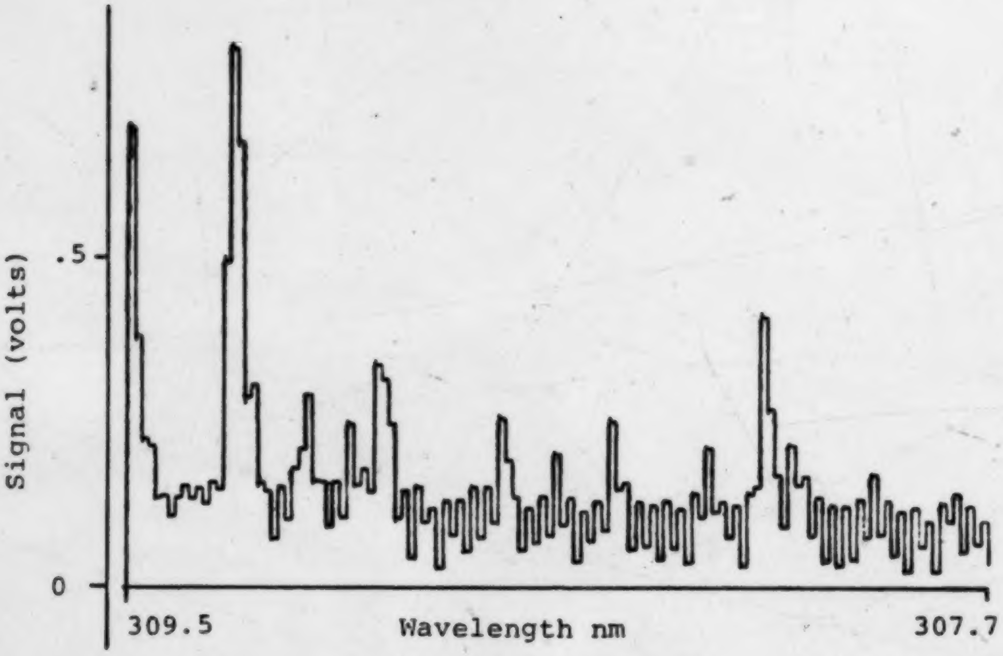
The odd-even pattern of the array must be considered when calculating the background to be subtracted. One of the options in the peak height extraction program automatically considers the odd and even diodes as two separate populations.

An alternative method to remove the odd-even structure from the spectrum is the use of pair average smoothing. The effect of this is shown in Figure 59. If this technique is used it must be used consistently for both analyte and calibration runs. It does reduce the resolution of the spectrum.

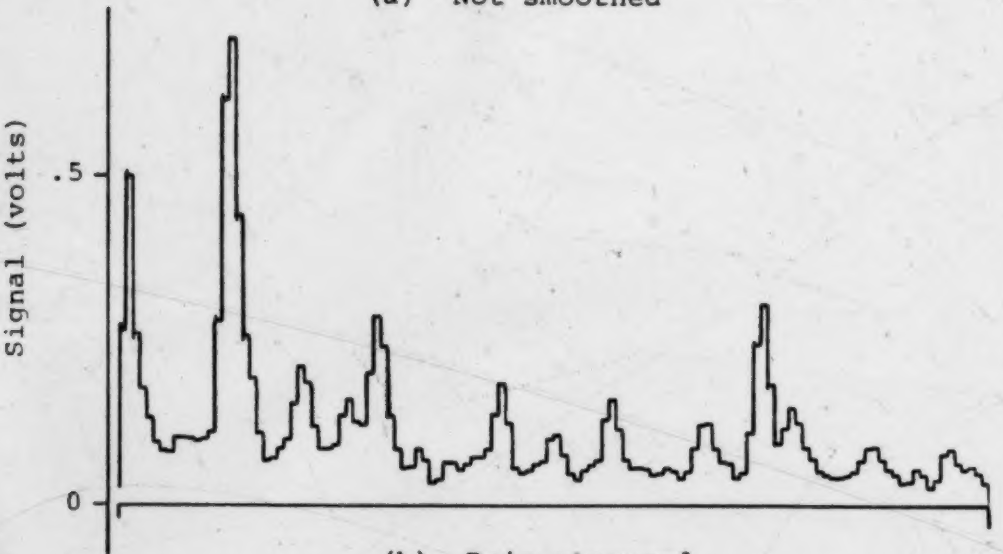
Continuous concomitant interferences such as recombination continua and scattered stray light are compensated for by the peak extraction program.

This concludes the description of the design, construction and use of a photodiode array direct reader. Its spectral windows have been used to remove many of the limitations of the photomultiplier tube based instruments.

In particular it compensates for spectral interferences and imparts versatility. In doing so it restores to spectroscopic analysis the more favourable



(a) Not smoothed



(b) Pair averaged

Figure 59. The smoothing effect of pair averaging on the odd-even pattern.

characteristics of the photographic method that were sacrificed in the cause of electronic readout.

This instrument is still only a step along the way to an optimized electronic imaging direct reader. The basic principles have been explored and put into practice within the limits of the equipment made available. The present design is not perfect and there are several problems to solve before the perfect instrument can be built. Some of these have been discovered during the development of this system and are described in Chapter VII.

CHAPTER VII

UNSOLVED PROBLEMS AND DIFFICULTIES

The photodiode array direct reader constructed was a modular system. As a prototype it was assembled from components, most of which were designed for other purposes. Consequently a lot of compromises were necessary.

This chapter describes some of the difficulties encountered and not fully solved. The instrument has great potential but further work is necessary to improve the mechanical, electronic and optical characteristics. Some of the problems are a function of this one particular instrument and now that they are recognized could be designed out of any future instrument.

1. Alignment Problems

Due to its physical size, shape and weight, the light proof box of the direct reader could not be mounted on one of the standard optical rail beds that are used in our laboratory. It was mounted on a fixed stand. All alignment adjustments had to be made by physically moving and adjusting the optical rail bed carrying the spectral source and any external optics. Because the whole system was not on a single mounting, the alignment was easily lost. Complete redesign of a new instrument on a single mounting would eliminate this problem.

2. Illumination of the Grating

The diode array does not have the high signal gain of the photomultiplier tube and needs to receive as much of the signal generated by the source as possible. The f-number of the grating with respect to the entrance slit was 19.4 (grating width 6.3 cm and distance from the entrance slit 122 cm). The external optics controlling the illumination of the entrance slit should have a similar f-number. It was found experimentally that short focal length lenses (10-12 cm) gave no better illumination of the grating than those of longer focal length (25-30 cm). Although shorter focal length lenses could gather more of the emission from the source, they overfilled the grating and merely added to the stray light entering the system. The multi-array system was set up with a 30 cm focal length, 5 cm diameter, quartz lens, optimized with the lens 68 cm from the entrance slit and 50 cm from the plasma plume. Thus the image of the plasma plume was focussed 7 cm inside the entrance slit. The entrance slit was illuminated by light originating 10 to 23 mm above the load coil of the plasma source. A 5 cm diameter lens 50 cm from the source gives a small solid angle, gathering only 1 part in 1,600 of the light emitted by the source.

In a redesigned system with a single mounting, a collimating light collection lens could be used to gather more of the emission. A collimating lens 10 cm from the plasma plume would collect 25 times the light level collected by a lens at 50 cm. A more densely ruled grating with a smaller radius would maintain the reciprocal dispersion at the focal plane yet allow a lower f-number for the entrance optics.

3. Grating Defects

The light losses in the UV region due to inappropriate blazing of the grating were considerable. Second order intensities for the zinc 213.9 nm and cadmium 214.4 nm lines were six times the first order values. As additional evidence of the rapid deterioration of the grating output at short wavelengths, consider the simultaneous measurement of 10 ppm manganese at two different wavelengths.

Winge, Peterson and Fassel [43] give the detection limit ratio of the 403.08 nm and 279.48 nm lines as 3.5 to 1. The ratio found by the diode array direct reader was

0.12 to 1. The disparity between the two instruments involves a factor of 29 for measurements of two lines only 123 nm apart. This would suggest that the intensity loss for the zinc and cadmium lines is only partially regained by changing to second order.

A diffraction grating specifically blazed for the lower wavelengths required for the ICP should lower the detection limits in the ultraviolet region down to the photomultiplier tube detection limits. However, this would require experimental verification.

The ghost problem can be reduced by using a better quality grating.

One manufacturer [10] claims that a ruled grating should have a parent to ghost intensity ratio of 10^6 to 10^4, much better than the 133 of the grating used. The ghosts can be eliminated if a holographic grating is used. However the efficiency of such a grating is a function of wavelength divided by the grating line interval. They cannot be easily blazed for efficiency like a ruled grating can. It is claimed [10] that a holographic grating is most efficient for wavelengths 1.7 to 0.8 times the grating interval. Thus a holographic grating with 4,000 lines per mm would have its peak efficiency in the wavelength range 200 to 425 nm. Holographic gratings are available with up to 6,000 lines per mm.

4. Stray Light Introduced by the Circuitry

The photodiode array direct reader has a considerable amount of circuitry mounted inside the dark box. This is necessary as the RC1024S drive boards have to be close to the diode arrays. Although the mounting boards are blackened, there is a considerable amount of circuitry with reflective surfaces (see Photograph 3). The diode arrays are in the focal plane of the direct reader and any light reflected back, from the metal surrounding the diodes, towards the grating will be refocussed elsewhere on the focal plane. If the wavelength of the reflected light is long enough secondary diffraction can occur and interfere at lower wavelengths. Greater interference would be expected from the reflected light refocussed by the unruled portion of the grating blank.

A finely divided coating of ice builds up on the ends of the array cooling bars. This acts as a diffuse reflector for light falling on it, adding to the stray light in the system.

Light falling on the circuitry behind the focal plane will not be sharply focussed. Furthermore, any light reflected back to the grating will be refocussed inside the Rowland circle and hence will be out of focus at the focal plane to give general stray light rather than sharp lines.

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Photograph 3. The focal plane area with six diode arrays fitted.

No major stray light problems have been observed but they are possible. Reflections off the array surrounds would be hard to reduce although their effect might be reduced by masking the unruled portion of the grating blank. If the reflection occurs behind the array it can be reduced by covering the offending circuitry with black velvet.

5. Limitations on Spectral Window Selection

The width of the sensing part of the 128 diode array is 3.2 mm. The array chip itself is 27 mm wide and the mounting carriage width is 43 mm. Consequently there are strict limitations on the selection of spectral windows as only about 7% of the spectral width occupied by the carriage can be sampled. Once a window has been selected, the next window has to be at least 25 nm away from it.

Diode arrays are available, in the same series, with 512 and 1024 diodes. The 1024 diode array has a sensing width of 25.6 mm and will fit on the same carriage. This gives a spectral window 14 nm wide with a 60% coverage of the width of the carriage. If this is still insufficient coverage of the spectrum, plane mirrors can be used to reflect the light into an array mounted in a different plane. The software is easily modified to allow for the readout of a larger array of diodes but it will force an increase in the minimum integration time.

Because the diode arrays are planar and the Rowland circle is curved, parts of the array are always out of focus. With the 1024 diode array this amounts to 0.1 mm focussing error for a 150 cm diameter Rowland circle and 0.2 mm error if a 75 cm diameter Rowland circle were to be used.

6. Possible Blooming Problems

If two lines of very different intensities fall close together on the same array, there may be some blooming problems. Talmi and Simpson [23] describe blooming effects in diode arrays as sequential overspill from diode to diode so if a weak line is too close to a very intense line, the diode saturation of the latter could wipe out the weaker line. Busch and Benton [57] describe this as a drawback of the diode array detector. This, however, overlooks the versatility of the array system. If one line is saturated by a much stronger neighbour, another analyte line must be selected.

There are very few elements that do not offer a selection of analytical lines with the inductively coupled plasma. If there is no alternative the edge of the array or a mask over part of the array may have to be used to selectively cut out the stronger line.

7. The Dark Current Problem

When the decision was made to use the smaller Peltier coolers for the six array system, it was considered that this would cool the back of the arrays to -21°C and that this would be cool enough. However, several of the arrays are obviously inadequately cooled. This shows up for integration times of 10 seconds or more as single diode glitches (Figures 57 and 58) and in one case as a major dark current artifact. These abnormalities are generated on the array, by the array, as they are diode specific and are probably due to manufacturing defects. As larger Peltier coolers would require a considerable increase in the DC power required to drive them, further cooling could be achieved by replacing the cooling water with a chilled fluid cooled in a closed system by refrigeration. In order to maintain flexibility, it may be necessary to change the type of coolant distribution hoses used. If the cooling fluid is too cold, the hoses may become coated with condensation or ice.

There may be another factor contributing to the cooling problem. The diode arrays are held in place by their 22 pins in their sockets. The arrays are cooled by the cold bar of their coolers through a thermally conducting paste. Heat transfer from the array is improved if the conducting paste film is made as thin as possible and this requires pressure. The only pressure acting on the arrays, to push them onto the cold bar, is exerted by the black plastic mask fitted to contain the dry nitrogen flow. This pressure is transmitted to the array through small pieces of sponge rubber which may or may not retain their elasticity at low temperatures. When the array is cooled and later allowed to warm up to room temperature, there will be an expansion-contraction problem caused by the use of different materials for the cooling bar, socket and mask. This may cause the array to work away from the cold bar. A review of the design of this heat transfer system should be considered as a first step in the reduction of the dark current problem. Because the peak evaluation techniques utilize measurements of values for off-peak diodes, it is important that the dark current be limited not only to allow sufficient signal dynamic range, but also to reduce the diode to diode dark current variation. This latter adds to the uncertainty of the background values.

According to Vogt [25], when the dark current exceeds about 5% of the diode saturation readout value, the shot noise in the thermal leakage becomes the dominant source of noise. This does not appear to be the case for the direct reader as its background variability is much greater than that which could be generated by dark current shot noise.

The dark current shot noise N_d (in electrons) is given by:-

$$N_d = \left(\frac{I_d . t_i}{q_e}\right)^{1/2}$$

where I_d is dark current, t_i is integration time in seconds and q_e is the charge on an electron in coulombs.

Talmi and Simpson [23] quote a value for N_d of 545 electrons rms at -20°C for a 1 second integration time. This would give 5,450 electrons rms shot noise for 100 seconds integration time. As the full 14 pC saturation charge on a diode is equivalent to 87.5×10^6 electrons, the dark current shot noise at -20°C for 100 seconds is very small (0.000062 times the saturation charge). This is equivalent to 62 μV noise on a 1 V signal or 3 times the least significant bit value of the AI13 analog to digital converter in the lowest (0 to 0.1 V) range. During the single array experiment, the lowest values of the readout noise were of the order of 1 mV at -28°C. This is much greater than the dark current shot noise.

However, shot noise is not the only cause of dark current variation. Over long integration periods temperature variation is more important. Consider the temperature change ΔT which would cause a dark current change equal to the readout noise N_r.

$$\Delta T = \frac{6.7\ N_r}{t_i . I_d .\ \ln 2} \text{ in °C [23]}$$

where N_r is in coulombs, t_i is integration time in seconds, and I_d is dark current. (The 6.7 and ln 2 terms refer to the doubling of dark current for a 6.7°C rise in temperature.)

At -20°C the dark current is 47 fA [23]. If the readout noise is 1 mV, equivalent to 87,500 electrons or 1.4×10^{-14} C, then ΔT has a value of 0.029°C, for 100 s integration. The Peltier coolers have to pump down the array temperature by 34°C, so they have to have long term voltage stability of below 0.08% to maintain such temperature control.

The Peltier cooler is not an absolute cooler, it is simply a pump transferring heat from the array (and the atmosphere) to the cooling water.

Over several seconds of integration time, the temperature of the cooling water could be affected by other users of the same water supply. Furthermore, because it is heated by the Peltier coolers, any change in water pressure resulting in change in flow rate would result in a change in its effective temperature. A temperature change in the cooling water of more than 0.03°C appears quite probable for a series of measurements taking several minutes. This may be a contribution to the increase in noise observed for the single array system as integration times were increased to 16 and 32 seconds (Table 7).

Vogt [25] also describes the generation of hole-electron pairs, and hence dark current, by power dissipation within the array chip during readout. This is another possible source of variation in the dark current although the change may not be significant with long integration times where the heat produced is not allowed to accumulate.

The noise generated by temperature changes is directly proportional to the time integrated dark current and would be reduced by operating the array at lower temperatures.

8. Problems Caused by the Ribbon Cable

The layout of the RC1024S array drive boards meant that the arrays had to be run away from their drive boards. Twenty one of the array chip's pins are functional and must be connected to the drive board. The number of leads might have been reduced by 5 by combining common functions but this still leaves too many to handle by shielded cables yet still retain some freedom of movement for the array. Consequently a ribbon cable was used. This was soldered to the back pins of the array socket on the array carriage and to a makeshift plug to fit into the onboard socket. Unfortunately the array is in the form of a 22 DIP chip and although 22 pin sockets were available, 22 pin DIP plugs were unobtainable. The 22 pin DIP chip is the only size of integrated circuit that has its 2 rows of pins separated by 0.4 inches. It was found that solder tail 22 pin sockets could act as plugs and these were used for the ribbon cables. They do not have the same conductor contact within the socket as one would expect from plugs.

Apart from the already described signal loss and cross-coupling of signals along the cable, there was some evidence of variability between even and odd diode signals depending on the position and degree of twist in the ribbon cable. This meant that the final tuning of the array circuitry had to be carried out after the array had been fixed in its correct position in the direct reader focal plane.

The ribbon cable is the weak link of the system and occurs at its most vulnerable spot, before the signals from the array have been amplified. It would be far better to replace the existing drive board and the ribbon cable with a redesigned printed circuit board carrying the array transversely at one end.

9. Problems Associated with the RC1024S Drive Board

When the drive board, modified as described in Chapter III, was used with the single array system, the only major problem experienced was the drifting of the odd-even diode balance with time. For a single array this was easy to follow and correct.

When all six arrays were running, several more serious defects were noticed. No two array systems were exactly alike. One system had an odd-even balance that varied too much to be useful. Another system had an unstable background level that prevented its use for integration times longer than 0.5 seconds. Another had an odd-even balance problem that affected the first few diodes only (Figures 50 and 51).

The variation in the DC background level was more than that which occurred with the single array system. This variation was often sufficient to move the signal out of range of the analog to digital converter, especially when the latter was operating on its lowest input range setting.

An example of an oscillation occurring within the odd-even balance circuitry is shown in Figure 60. The oscillation was independent of the diode number and the start pulse so must have been generated on the RC1024S drive board.

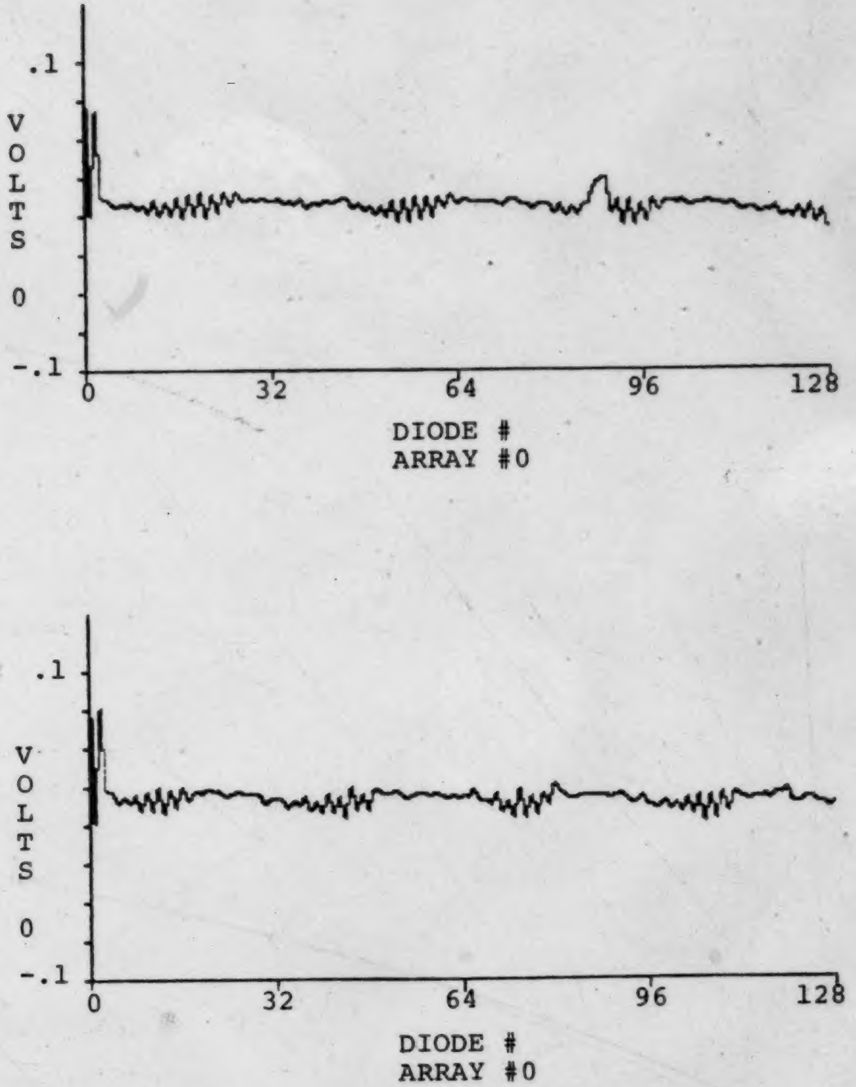


Figure 60. Pattern produced by oscillation in the odd-even balance circuit.

The major problem that arose was the frequently obtained excess in signal strengths at the output of the RC1024S board as illustrated by Figure 61. The odd-even balance appears to be unaffected which indicates that the signal gain occurred before the odd-even balance adjustment was applied.

The signal processing system is shown in Figure 62. The excess gain applies to both odd and even diodes so the cause must apply equally to both halves of the signal processing circuitry. A power supply variation is a possibility. Alternately, the signal change could be due to gross changes in the nebulizer throughput. This is highly unlikely but could be checked by the use of a pumped nebulizer. Calculations for the expected strength of the signal favour the low values.

This problem prevented the use of signal averaging and slowed down the gathering of data as every data set had to be checked for the excess by displaying it graphically on the video monitor.

The power supply driving the 6 array boards was tested at the input to one of the boards with all of the boards powered. The +5 V supply had high frequency background noise superimposed on a 4 mV peak to peak variation of 10 kHz frequency. The +15 V supply had a 5 mV peak to peak signal at a 200 kHz frequency with a spike

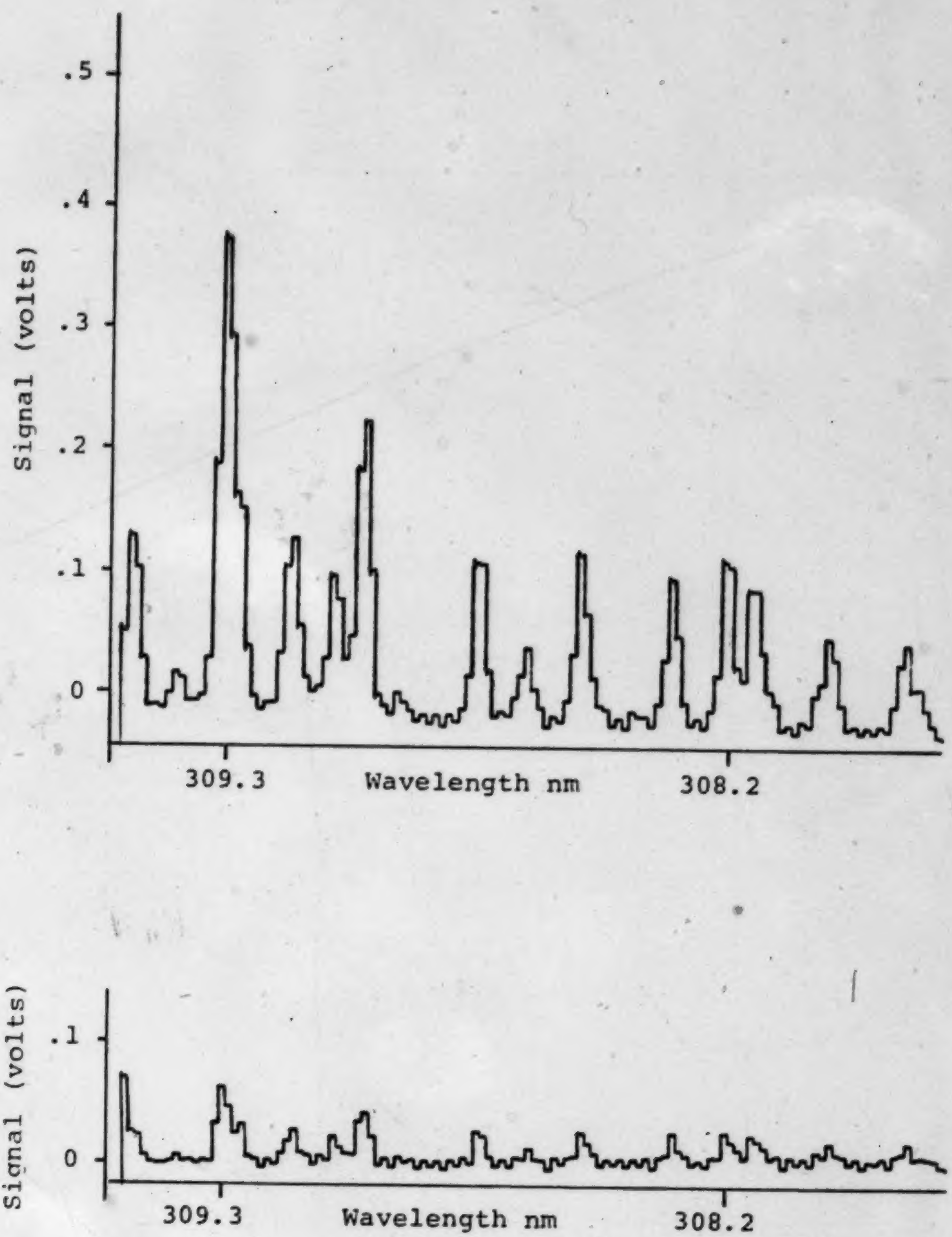
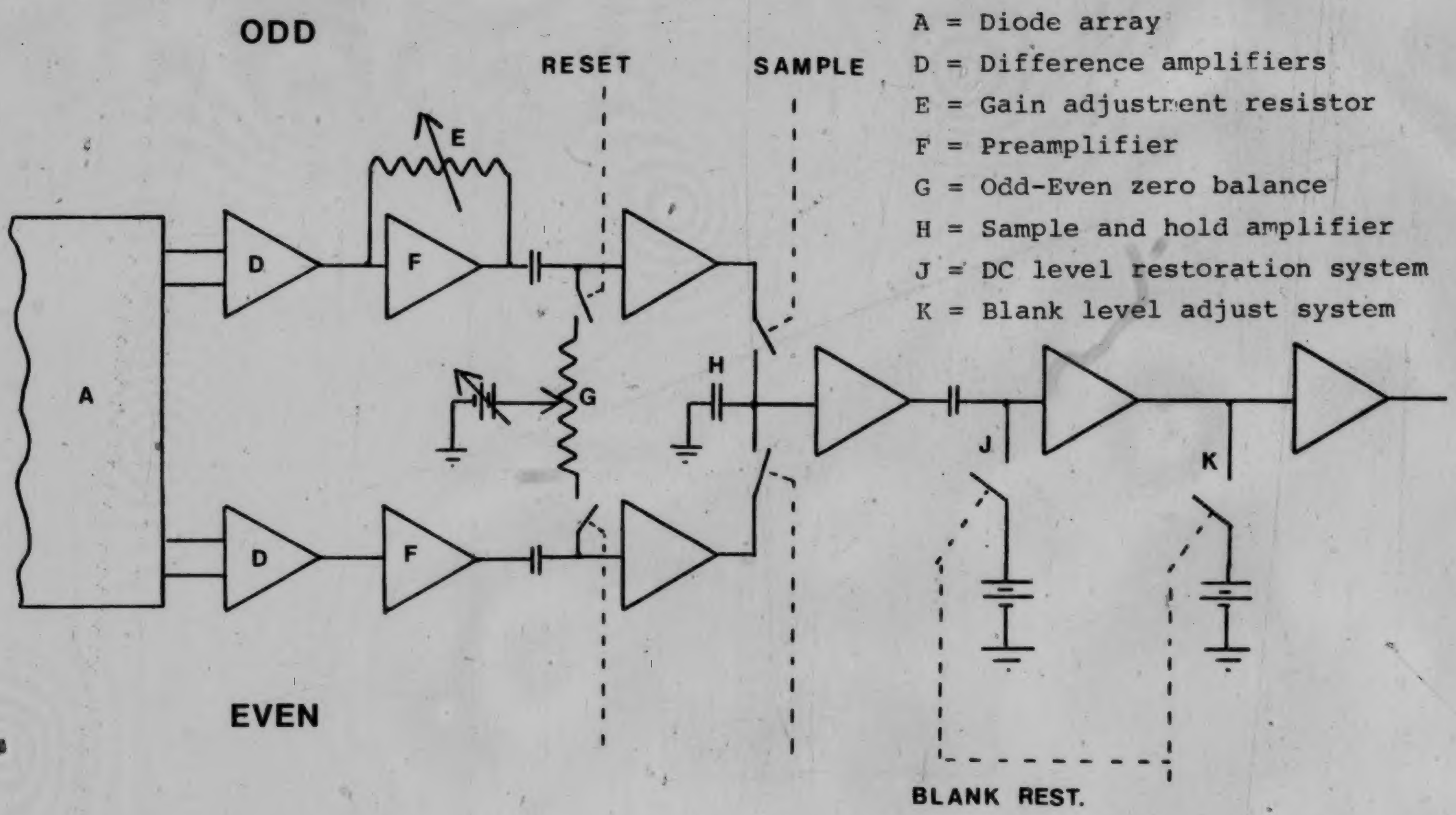


Figure 61. Variation in the signal output from the RC1024S board for two identical signal measurements (10 seconds integration).


ODD
EVEN
RESET
SAMPLE
A
D
D
E
F
F
G
H
J
K
BLANK REST.

A = Diode array
D = Difference amplifiers
E = Gain adjustment resistor
F = Preamplifier
G = Odd-Even zero balance
H = Sample and hold amplifier
J = DC level restoration system
K = Blank level adjust system

Figure 62. Diagram of the signal processing circuit for a photodiode array.

superimposed at 10 kHz. The -15 V supply had a square wave pattern of 10 mV peak to peak at 10 kHz together with higher frequency background noise. The square wave disappeared when all the array systems but one were uncoupled from the power supply.

The direct reader system used three power supplies, excluding those used to drive the Peltier coolers. The system should be redesigned to run off a single power supply. In this respect it should be noted that there are significant differences in the ground levels of the electrical service outlets. For example, a 30 mV difference was measured across the ground wires of two cables fed from the same circuit breaker.

The cause of the readout variations has not been established and further work is required.

10. Precision Limitations of the System

The precision of one of the arrays in the six array system was determined from 10 measurements for a solution of 1.5 ppm copper. The results are given in Table 23. The background means and standard deviation for each determination were obtained from values of 8 off-peak diodes of the same odd-even character as the peak diode. The background standard deviations are approximately 1 mV, which is of the same order as those found for the single array system.

Table 23. Measurements of precision for 1.5 ppm copper solution.

Peak Height V	Background Mean V	Background Std. Deviation	Signal/Noise
.01001	.05171	.00096	10.5
.00854	.04832	.00128	6.7
.00986	.05061	.00111	8.8
.00894	.05077	.00060	15.0
.00784	.05139	.00118	6.6
.00922	.05089	.00153	6.0
.00906	.05124	.00082	11.1
.0085	.0506	.00135	6.3
.00847	.05134	.00105	8.0
.0086	.05072	.00107	8.0

Mean peak height for 10 runs 0.00890 V.

Standard deviation between 10 runs 0.000664 V.

Ratio 13.4.

Background mean standard deviation between runs 0.00094 V.

The signals from the spectral source, processed by the array and its drive board, are digitized by the analog to digital converter and stored by the computer. Measurements were made of the variability of the data acquisition system by grounding the input lines to the pre-amplifiers of the AI13 analog to digital converter and recording the digitized values for 128 successive conversions for all 6 channels in use. The diode array sampling pulses were used to initiate the conversions. The effect of signal averaging was also determined. Results are summarized in Table 24. The least significant bit value for each A/DC setting is included for comparison.

As the signal averaging technique reduced the variability, the latter can be considered to be generally due to random noise. The variability for a single set of measurements, albeit for a large set, of about half a millivolt is approaching the variability for the overall signal measurement (Table 23). Consequently, any new design to improve the precision of the whole system must use a more stable A/DC. There are 2 probable reasons for the A/DC variations.

i. The A/DC and the preamplifiers are powered by the Apple power supply which is involved in driving many TTL logic changes and hence is very noisy.

Table 24. Variability of the AI13 data acquisition system.

	Standard deviations (V) A/DC range settings of			
Run Multiple	± .1 V	± .5 V	± 1 V	± 5 V
1	4.95×10^{-4}	8.79×10^{-4}	2.98×10^{-3}	2.76×10^{-3}
10	2.59×10^{-4}	2.57×10^{-4}	9.39×10^{-4}	1.11×10^{-3}
100	7.17×10^{-5}	1.21×10^{-4}	3.49×10^{-4}	1.16×10^{-3}
LSB	4.88×10^{-5}	2.44×10^{-4}	4.88×10^{-4}	2.44×10^{-3}

ii. The analog signals are carried by a ribbon cable into the Apple case and the actual A/DC is not shielded against interference from the other electronic transitions occurring nearby.

In order to improve the precision for the same illumination of the grating, the noise levels must be reduced.

A 1 mV noise level is equivalent to one thousandth of the saturation signal of the array or 87,500 electrons rms. Simpson [31] has described the various noise sources for the S series of photodiode arrays. These are:-

i. The photon shot noise of the incident light.
ii. The shot noise of the dark current.
iii. Preamplifier noise.
iv. Reset noise of the diodes of the array.

Of these the photon shot noise is common to all detection systems.

The dark current shot noise has already been discussed. It has rms values of 5,600 × $\sqrt{t_i}$ at 25°C and 545 $\sqrt{t_i}$ at -20°C where t_i is integration time in seconds [23].

The diode reset or thermodynamic noise n_r is given by [31]

$$n_r = \left(\frac{1}{q_e}\right)[kT(2C_p + 2C_{vc})]^{1/2}$$

where k is the Boltzmann Constant, T is absolute temperature, C_p is the diode capacitance, C_{vc} is video line to clock line capacitance and q_e is the charge on the electron.

Simpson quotes a value of 1000 electrons rms for n_r at 25°C for a 1024 diode array.

The preamplifier noise is given by [31]

$$n_a = \left(\frac{1}{q_e}\right)\left[(i_n\ t_p)^2 + (e_n C)^2\right]^{1/2}$$

where i_n is the preamplifier noise current, e_n is the preamplifier input noise voltage, C is capacitance at the amplifier input and t_p is the time to read a diode.

Simpson states: "With the proper choice of input device and circuit design, n_a can be reduced below the thermodynamic noise." That is to say below 1000 electrons rms.

Thus the total noise for dark current and readout could be as low as

$$n_T = (10^6 + 10^6 + 31 \times 10^6 \times t_i)^{1/2} \text{ at } 25°\text{C}$$

This gives n_T equal to 5,775 electrons rms for a 1 second integration and 55,695 electrons for a 100 second integration. At -20°C a 100 second integration time could have a noise level as low as 5,620 electrons rms. The direct reader system has 87,500 electrons rms noise. Unlike the systems described by Simpson, the direct reader noise is limited by readout noise, not the dark current shot noise. The designers of the RC1024S have taken care to limit the distance between the array and the preamplifier as the equations for both the thermodynamic noise and the preamplifier noise contain capacitance terms. Clearly no great improvement in the precision of the diode array direct reader can be expected until the ribbon cable is replaced by a redesigned drive card.

Several discussions of low noise ampifiers for diode arrays can be found in the published literature [25,26,31,58].

11. Processing Delays Caused by Program Loading

The software to run the direct reader system was written and operated in sections to suit the experimental nature of the system. The Apple disk operating system is designed so that the disk drives are normally off. This is done to save wear. However, there is some delay caused by the system requiring time to start up. During the development of the direct reader, the operation of the disk drives has been a useful diagnostic tool.

For a routine operating system, a faster running system would be preferred. The overall speed of operation could be improved in several ways:-

i. All machine code programs could be located in the 16K language card and called when required. In order to save loading them at every start up they could be loaded onto a read only memory chip which is then fitted to the language card.

ii. Basic programs used sequentially could be combined. Programs can be shortened by leaving out REM statements, combining lines and becoming less user friendly.

iii. Faster running disk operating systems are available.

iv. Some of the BASIC routines such as multiplication and division could be duplicated in machine code and loaded into the language card.

The problems associated with the diode array direct reader are considerable but all are capable of solution. They are worth solving because the potential of the instrument is considerable. Photodiode array detectors are already in use as full spectrum detectors for ultraviolet and visible molecular absorption spectroscopy [59]. Their application in commercial instruments for atomic emission spectroscopy is overdue.

BIBLIOGRAPHY

1. Harrison, G.R., "Some future possibilities of spectrographic analysis", Conference on spectroscopy and its applications, Cambridge, Mass., 1940.
2. Duffendack, O.S.; Morris, W.E., J. Opt. Soc. Amer., 1942, 32, 8-24.
3. Saunderson, J.L.; Caldecourt, V.J.; Peterson, E.W., J. Opt. Soc. Amer., 1945, 35, 681-697.
4. Hasler, M.F.; Dietert, H.W., J. Opt. Soc. Amer., 1944, 34, 751-758.
5. "Spex Methods for Semiquantitative Spectrochemical Analysis", Monograph, Spex Industries Inc.
6. Boumans, P.W.J.M., Optica Pura Y Aplicada, 1978, 11, 143-171.
7. Barnes, R.M. in "Instrumental Analysis"; Bauer, H.H.; Christian, G.D.; O'Reilly, J.E., Eds., Allyn and Bacon, Inc. p 317, 1978.
8. The JY 70P spectroanalyzer", Monograph by Jobin Yvon Division of Instruments S.A., Longjumeau, France.
9. Larson, G.F.; Fassel, V.A.; Winge, R.K.; Kniseley, R.N., Appl. Spectrosc., 1976, 30, 384-391.
10. "Diffraction Gratings, Ruled and Holographic", monograph by Jobin Yvon Division of Instruments S.A., Longjumeau, France.

11. Davis, S.P., "Diffraction Grating Spectrographs", Holt, Rinehart and Winston, 1970.

12. Larson, G.F.; Fassel, V.A., Appl. Spectrosc., 1979, 33, 592-599.

13. Sobel, H.R.; Dahlquist, R.L., American Laboratory, 1981, 13, 152-157.

14. Ward, A.F.; Marciello, L.F., Anal. Chem., 1979, 51, 2264-2272.

15. Spillman, R.W.; Malmstadt, H.V., Anal. Chem., 1976, 48, 303.

16. Blades, M.W.; Horlick, G., Appl. Spectrosc., 1978, 34, 303.

17. Brehm, R.K.; Fassel, V.A., J. Opt. Soc. Amer., 1953, 43, 886.

18. Perruli, B.D.; Katzenberger, J.; Lerner, J.M., The Pittsburgh Conference, Atlantic City, N.J., March 1980.

19. Wood, D.L.; Dargis, A.B.; Nash, D.L., Appl. Spectrosc., 1975, 29, 310.

20. McGeorge, S.W.; Salin, E.D., Can. J. Spectrosc., 1982, 27, 25-36.

21. Busch, K.W.; Malloy, B., in "Multichannel Image Detectors", Talmi, Y. Ed., ACS Symposium Series 102, American Chemical Society, Washington, D.C., 1979, pp 27-58.

22. Talmi, Y, in "Multichannel Image Detectors", Talmi, Y. Ed., ACS Symposium Series 102, American Chemical Society, Washington, D.C., 1979, pp 3-25.

23. Talmi, Y.; Simpson, R.W., Appl. Optics, 1980, 19, 1401-1413.

24. Horlick, G., Appl. Spectrosc., 1976, 30, 113-123.

25. Vogt, S.S.; Tull, R.G.; Kelton, P., Appl. Optics, 1978, 17, 574-592.

26. Livingston, W.C.; Harvey, J.; Slaughter, C.; Trumbo, D., Appl. Optics, 1976, 15, 40-52.

27. Rowland, H.A., Phil. Mag., 1882, 13, 469.

28. Sawyer, R.A., "Experimental Spectroscopy", Prentice Hall, 1951, p 132.

29. Horlick, G.; Codding, E.G., "Photodiode Arrays for Spectrochemical Measurements", in Contemporary Topics in Analytical and Clinical Chemistry, Vol. I, Hercules, D.M., Ed., Plenum Press 1977.

30. "S-series solid state line scanners", Technical brochure, EG & G Reticon, 1978.

31. Simpson, R.W., Rev. Sci. Instrum., 1979, 50, 730-732.

32. Technical Brochure, "Frigichip Miniature Ceramic Modules", Materials Electronic Products Corp., Trenton, N.J.

33. Betty, K.R.; Horlick, G., Anal. Chem., 1977, 49, 342-345.

34. Fairchild Semiconductor TTL Data Book, Fairchild Semiconductor, Mountain View, CA.

35. Data-Acquisition Databook, 1982, Analog Devices, Norwood Mass. 1, Section 14, 30.

36. Handbook of Operational Amplifiers, Active RC Networks; Burr Brown Research Corporation, Tucson, Arizona, 74.

37. Coleman, D.M.; Walters, J.P., Spectrochim. Acta, 1978, 33B, 127.

38. Publication #66-000-1M, Jarrell Ash Division of Fisher Scientific Company, Newtonville, Mass.

39. Salin, E.D.; Horlick, G., Anal. Chem., 1980, 52, 1578-1582.

40. Horlick, G.; Codding, E.G., Anal. Chem., 1973, 45, 1490.

41. Hog, E.; Wiskott, D., European Southern Obs. Tec. Report #5 (November 1974).

42. Kubota, M.; Fujishiro, Y.; Ishida, R., Spectrochim. Acta, 1982, 37B, 849-857.

43. Winge, R.K.; Peterson, V.J.; Fassel, V.A., Appl. Spectrosc., 1979, 33, 206-219.

44. Hull, D.R., Jarrell Ash Company, May 1981, private communication.

45. Keliher, P.N.; Wohlers, C.C., Anal. Chem., 1976, 48, 333A.

46. Greenfield, S.; Jones, I.L.; Berry, C.T., Analyst, 1964, 89, 713.

47. Wendt, R.H.; Fassel, V.A., Anal. Chem., 1965, 370, 920.

48. Karanassios, V., University of Alberta, November 1981, private communication.

49. Blades, M., Ph.D. Thesis, Department of Chemistry, University of Alberta, 1981.

50. Bongers, C., Nibble, 1982, 3, #4, 127-137.

51. Forster, A.R.; Anderson, T.A.; Parsons, M.L., Appl. Spectrosc., 1982, 36, 499-504.

52. Warme, P.K., "Curve Fitter", Interactive Microware Inc., State College, Pa.

53. Harrison, G.R., J. Opt. Soc. Amer., 1949, 39, 522-528.

54. Dieke, G.H.; Crosswhite, H.M., J. Quant. Spectrosc. Radiative Transfer, 1962, 2, 97-199.

55. Pearse, R.W.B.; Gaydon, A.G., "The Identification of Molecular Spectra", Chapman and Hall, London, 1965, 3rd Edition, p 227.

56. Seto, J., M.Sc. Thesis, Department of Chemistry, University of Alberta, 1982.

57. Busch, K.W.; Benton, L.D., Anal. Chem., 1983, 55, 445A-460A.

58. Buss, R.R.; Tanaka, S.C.; Weckler, G.P., in "Solid State Imaging", Jespers, P.G., Ed., NATO Advanced Studies, Noordhof, Leyden, 1976.

59. Anal. Chem., 1983, 55, 465A.

60. The DOS Manual for the Apple II, Apple Computer INC., p 151.

61. Fassel, V.A.; Kniseley, R.N., Anal. Chem., 1974, 46, 1155A.

The following publications, not specifically referred to in the thesis, were of great assistance during the work.

62. R6500 Microcomputer System Hardware Manual, Rockwell International Corporation.

63. R6500 Microcomputer System Programming Manual, Rockwell International Corporation.

64. Logic Data Book, National Semiconductor Corporation.

65. A113 Analog Input System Users Manual, Interactive Structures Inc.

66. The 8080 Microcomputer System Users' Manual, 1975, Intel Corporation.

67. Apple II Reference Manual, Apple Computer Inc.

68. Applesoft II Basic Programming Reference Manual, Apple Computer Inc.

69. Applesoft Tool Kit, Apple Computer Inc.

70. Apple 6502 Assembler/Editor, Apple Computer Inc.

APPENDIX 1

APPENDIX 1

THE INDUCTIVELY COUPLED ARGON PLASMA SOURCE

The plasma spectral source was a Plasma-Therm ICP 2500 powered by a Model HFP 2500 F, 2.5 kW RF generator (27.12 MHz).

The plasma torch was made by the Department of Chemistry glass blowing shop at the University of Alberta. It consisted of 3 concentric quartz tubes fused together as described by Fassel and Kniseley [61]. The outer, plasma gas, tube had an internal diameter of 18 mm. The next, auxiliary gas, tube had an internal diameter of 12 mm. The central, aerosol, tube was 3 mm internal diameter, constricted down to 1.5 mm at its exit.

The plasma torch was attached to a spray chamber supplied by Plasma-Therm. Several nebulizers were used; all were the glass concentric (Meinhard) type with aspiration rate of 0.6 to 1.0 ml per minute.

The argon flow rates were:-

i. Plasma gas - 13 lpm
ii. Nebulizer gas - .65 lpm (Chapter IV)
  - .4 lpm (Chapter VI)

- 15 psi (Chapter VI)

iv. Auxiliary gas - .8 lpm (Chapter IV)

- .4 lpm (Chapter VI)

- .6 lpm (Chapter VI)

✓

APPENDIX 2

APPENDIX 2

MODIFICATION OF THE RC1024S CIRCUIT BOARD

A. Join Edge Tab 6 to Edge Tab F

Tab 6 carries the odd diode series end of line signal (Diode 127 has been read). Pin 6 on the 44 pin edge connector interfered with the firm attachment of the coaxial cable carrying the output signal from the board. Pin 6 was then removed from the edge connector leaving the odd EOL signal available on pin F.

B. Change Capacitor C_1

Capacitor C_1 is a timing capacitor in the oscillator. It was changed from 500 pf to 0.005 μf to reduce the diode sampling rate range from 37.5-150 kHz to 4-62.5 kHz.

C. Connect Edge Tab W to OR'd Sampling Pulse

Pins 9, 10, 11 of U30 (7400) on the board carry the OR'd odd and even sampling pulse signals. The signal was wired to edge tab W so that it could be used elsewhere as a data acquisition control signal.

D. Rewire Pin 3 on 7474 Flip-Flop

Flip-flop U11 (7474) is the start pulse controller. The printed circuit lead to pin 3 was cut to isolate it from the onboard timing chain. It was wired to edge tab R to connect it to the off board start pulse generator.

E. Isolate the Oscillator

The output of the oscillator was isolated from the rest of the circuit so that it could be gated. The printed circuit was cut between pin 5 on U1 (9602) and pin 1 on U6 (7404). It also separated it from pin 2 on U2 (74161), the first counter in the timing chain. The oscillator signal was already connected to edge tab U for connection to the gate.

F. Join Edge Tab P to U2 and U6

The gated oscillator signal was brought back to the board through edge connector P and hence to pin 1 on U6 (7404) and pin 2 on U2 (74161).

G. Remove the Last Onboard Counter

U5 (74161) the fourth 16 bit counter was replaced by a socket to connect to the timing chain extension. When external start pulses were introduced, the unused socket was bypassed by connecting its controlling enable pin to its overflow pulse pin (Pin 10 to pin 15).

H. Join Edge Tab M to Pin 5 of 7474 Flip-Flop

Pin 5 of U11 (7474) puts out the start pulse signal to the array. It was wired to edge tab M so that both the rising and falling edges of the start pulse were available as data acquisition control signals.

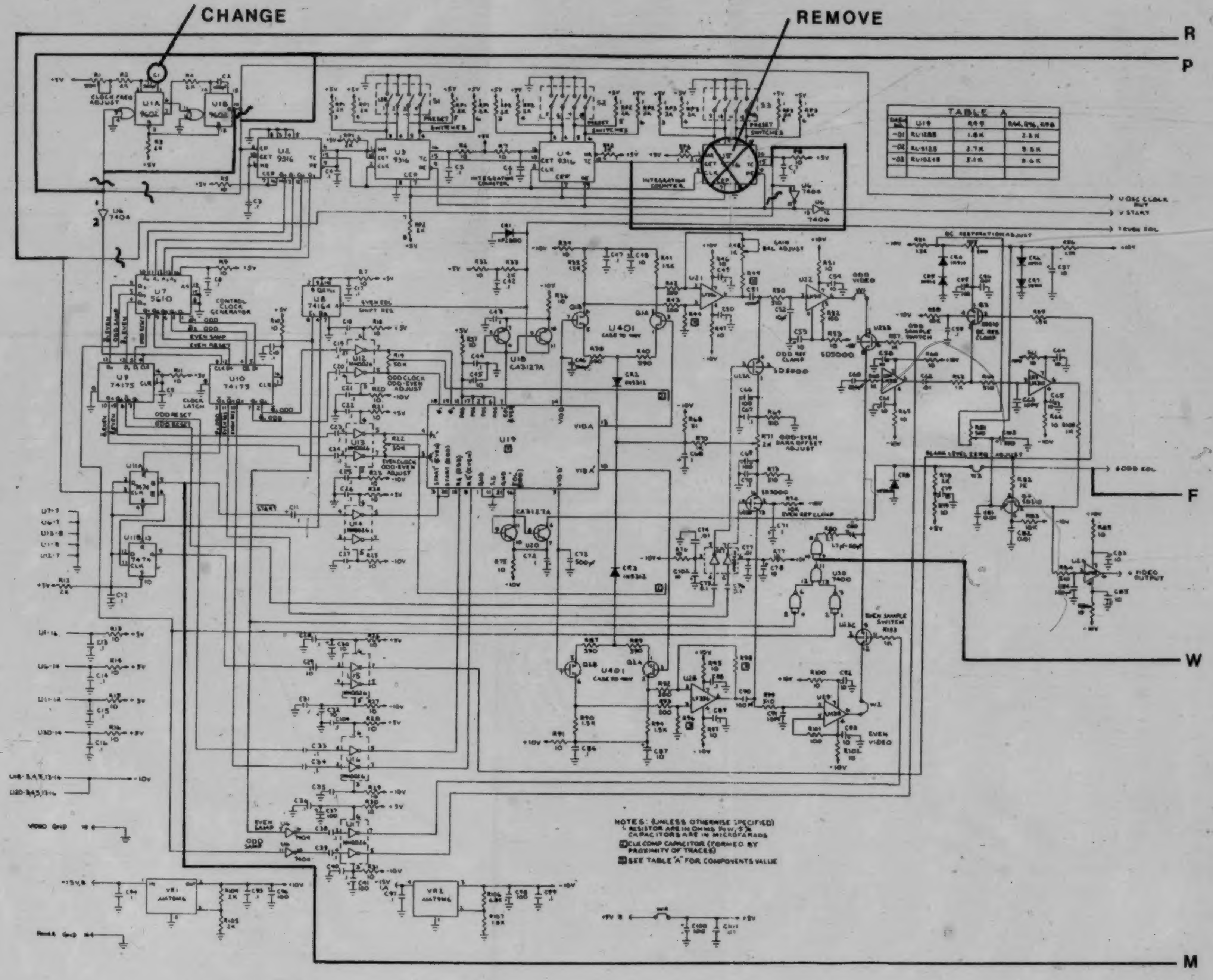

CHANGE
REMOVE
R
P
F
W
M
TABLE A
DASH NO. | U19 | R49 | R44, R76, R98
-01 | RL-128S | 1.8K | 2.2K
-02 | RL-512S | 2.7K | 5.5K
-03 | RL-1024S | 5.1K | 9.6K
NOTES: (UNLESS OTHERWISE SPECIFIED)
1. RESISTOR ARE IN OHMS ¼W, 5%
CAPACITORS ARE IN MICROFARADS
CLK COMP CAPACITOR (FORMED BY PROXIMITY OF TRACES)
SEE TABLE "A" FOR COMPONENTS VALUE
INTEGRATION COUNTER
PRESET SWITCHES
U19
U401
DC RESTORATION ADJUST
ODD-EVEN DARK OFFSET ADJUST
EVEN VIDEO
ODD VIDEO
VIDEO OUTPUT

Figure 63. Changes to the RC1024S board.

APPENDIX 3

APPENDIX 3

INTERFACE BETWEEN THE AIM 65 AND THE 1131J A/DC

AC 1580 CONNECTOR	
LINE	EDGE TAB
BIT 13	2
LSB (14)	3
TTY 14	4
TTY 10	5
TTY 5	6
TTY 1	7
START PULSE	13
DIGITAL GROUND	15
GROUND	22
MSB (1)	A
BIT 2	B
BIT 3	C
BIT 4	D

AIM 65 J1 CONNECTOR	
EDGE TAB	LINE
4	PA1
14	PA0
R	TTY KBD RETURN
S	TTY PTR RETURN
T	TTY KBD
U	TTY PTR
18	CB1
1	GROUND
1	GROUND
16	PB5
13	PB4
12	PB3
11	PB2

AC 1580 CONNECTOR	
LINE	EDGE TAB
BIT 5	E
BIT 6	F
BIT 7	H
BIT 8	J
BIT 9	K
BIT 10	L
BIT 11	M
BIT 12	N
MIKE SOCKET	W
EAR SOCKET	X
STATUS	Z

AIM 65 J1 CONNECTOR	
EDGE TAB	LINE
10	PB1
9	PB0
8	PA7
7	PA6
6	PA5
5	PA4
2	PA3
3	PA2
M	AUDIO OUT
L	AUDIO IN
20	CA1

CONVERT COMMAND	V

DATA ACQUISITION CONTROL SIGNAL

APPENDIX 4

APPENDIX 4

AIM 65 PROGRAMS

The data acquisition program LOG1 collects the 14 bit data values for 128 diodes. It gives the option of signal averaging by adding consecutive sets of data and then dividing by the number of sets added. It has the option of subtracting the same number of sets of data for a selected background condition. The machine code part of the program sets the data storage addresses to zero and then idles while it waits for a start pulse. It then logs data on receipt of a conversion completed signal from the analog to digital converter. Three 8 bit bytes are used for each diode, a low byte, a high byte and an overflow or carry byte (in case the summed data values exceed the capacity of the lower two bytes). The data bytes are stored consecutively, with all the low bytes in one group, the high bytes in another and the carry bytes in a third.

```
10  REM **AIM 65 PROGRAMME LOG1**
25  REM COLLECT DATA FROM A SINGLE ARRAY OF 128 DIODES WITH SIGNAL AVERAGING
30  REM  AND OPTIONAL BACKGROUND SUBTRACTION
40  PRINT "BACKGROUND SUBTRACTED ? Y=1,N=0"
50 O = 128:J = 3712:K = J + O:L = K + O:M = 2 * O:F = 234:H =  - 1:G = O + H
60 P = O * O
70  REM  J,K,L ARE BASE ADDRESSES FOR STORAGE OF LOW,HIGH,CARRY BYTES OF DATA
80  REM F=234=$EA=NO OPERATION TO CANCELL JUMP INSTRUCTION IN LINE 120
90  REM  IN LINE 130
100  INPUT A
110  IF A = 1 THEN 150
120  POKE 1710,76: POKE 1711,5: POKE 1712,7
130  REM THIS FORCES A JUMP TO THE END OF THE MACHINE CODE PROGRAM
140  GOTO 160
150  POKE 1710,F: POKE 1711,F: POKE 1712,F
160  PRINT "# OF RUNS ?"
170  INPUT B
180  POKE 3711,B: POKE 4,80: POKE 5,6
190  REM  MACHINE CODE PROGRAMME STARTS AT ADDRESS $650
200 X =  USR (I): REM CALL MACHINE CODE PROGRAM HERE
210  FOR N = G TO 0 STEP H
220 C =  PEEK (J + N):D =  PEEK (K + N):E =  PEEK (L + N)
230  PRINT "#";O - N;"=";(((E * M + D) * M + C) * 10) / (B * P)
240  REM THIS ASSUMES A 14 BIT A/DC WITH A 0-10 VOLT RANGE
250  NEXT N
260  PRINT "DONE ?Y=1,N=0"
270  INPUT R
280  IF R = 0 THEN 40
```

```
SOURCE FILE: MLOG1
0000:            1 *MACHINE LANGUAGE PROGRAMME FOR AIM 65 DATA LOGGING WITH
0000:            2 *BACKGROUND SUBTRACTION OPTION
----- NEXT OBJECT FILE NAME IS MLOG1.OBJ0
0650:            3          ORG  $0650
0650:D8          4          CLD
0651:78          5          SEI
0652:A2 7F       6          LDX  #$7F      ;LOAD DATA MEMORY SPACE
0654:A9 00       7          LDA  #$00      ;WITH ZERO'S
0656:9D 80 0E    8 BR1      STA  $0E80,X
0659:9D 00 0F    9          STA  $0F00,X
065C:9D 80 0F   10          STA  $0F80,X
065F:CA         11          DEX
0660:10 F4      12          BPL  BR1
0662:EA         13          NOP
0663:AC 7F 0E   14          LDY  $0E7F     ;# OF RUNS TO BE AVERAGED
0666:A9 00      15          LDA  #$00
0668:8D 0C A0   16          STA  $A00C     ;PCR SETS IFR FOR 1 TO 0 STEP
066B:AD 00 A0   17          LDA  $A000     ;CLEAR IFR BITS 3 & 4
066E:AD 0D A0   18 BR2      LDA  $A00D     ;CHECK IFR FOR FLAG ON
0671:29 10      19          AND  #$10      ;BIT 4 (CB1) START PULSE
0673:F0 F9      20          BEQ  BR2
0675:AD 00 A0   21          LDA  $A000     ;CLEAR IFR BIT 4
0678:AD 01 A0   22          LDA  $A001     ;CLEAR IFR BITS 0 & 1
067B:A9 00      23          LDA  #$00      ;SET DDRA AND DDRB
067D:8D 03 A0   24          STA  $A003     ;SO ORA AND ORB ARE
0680:8D 02 A0   25          STA  $A002     ;ALL INPUTS
0683:A2 7F      26          LDX  #$7F      ;SET COUNTER FOR 128 DIODES
0685:AD 0D A0   27 BR3      LDA  $A00D     ;SEARCH FOR CLOCK PULSE
0688:29 02      28          AND  #$02
068A:F0 F9      29          BEQ  BR3
068C:AD 01 A0   30          LDA  $A001     ;READ LOWEST 8 BITS OF DATA
068F:7D 80 0E   31          ADC  $0E80,X   ;ADD IT TO THE DATA
0692:9D 80 0E   32          STA  $0E80,X   ;ALREADY COLLECTED
0695:AD 00 A0   33          LDA  $A000     ;READ HIGHEST BITS OF DATA
0698:29 3F      34          AND  #$3F      ;CLEAN OFF THE TWO MSB'S
069A:7D 00 0F   35          ADC  $0F00,X   ;ADD IT TO THE DATA
069D:9D 00 0F   36          STA  $0F00,X   ;ALREADY COLLECTED
06A0:BD 80 0F   37          LDA  $0F80,X   ;READ THE CARRY FILE
06A3:69 00      38          ADC  #$00      ;ADD THE NEW CARRY IF PRESENT
06A5:9D 80 0F   39          STA  $0F80,X   ;UPDATE THE CARRY FILE
06A8:CA         40          DEX            ;DECREMENT THE DIODE COUNTER
06A9:10 DA      41          BPL  BR3       ;READ ANOTHER DIODE ?
06AB:88         42          DEY            ;DECREMENT REPLICATION COUNTER
06AC:EA         43          NOP
06AD:D0 BF      44          BNE  BR2       ;READ WHOLE ARRAY AGAIN ?
06AF:4C 06 07   45          JMP  FINISH    ;IF NO BACKGROUND SUBTRACTION
06B2:           46 *                        RETURN TO BASIC
06B2:00         47          BRK            ;TIME TO TAKE BACKGROUND DATA
06B3:AC 7F 0E   48          LDY  $0E7F     ;SET UP REPLICATE COUNTER
06B6:A9 00      49          LDA  #$00
06B8:8D 0C A0   50          STA  $A00C     ;PCR SETS IFR FOR 1 TO 0 STEP
06BB:AD 00 A0   51          LDA  $A000     ;CLEAR IFR BITS 3 & 4
06BE:AD 0D A0   52 BR4      LDA  $A00D     ;CHECK IFR FOR FLAG ON
06C1:29 10      53          AND  #$10      ;BIT 4 (CB1) START PULSE
06C3:F0 F9      54          BEQ  BR4
06C5:AD 00 A0   55          LDA  $A000     ;CLEAR IFR BITS 3 & 4
06C8:AD 01 A0   56          LDA  $A001     ;CLEAR IFR BITS 0 & 1
06CB:A9 00      57          LDA  #$00      ;SET DDRA AND DDRB
06CD:8D 03 A0   58          STA  $A003     ;SO ORA AND ORB ARE
```

```
06D0:8D 02 A0   59          STA  $A002      ;ALL INPUTS
06D3:A2 7F      60          LDX  #$7F       ;SET COUNTER FOR 128 DIODES
06D5:AD 0D A0   61 BR5      LDA  $A00D      ;SEARCH FOR CLOCK PULSE
06D8:29 02      62          AND  #$02       ;ON BIT 1 (CA1)
06DA:F0 F9      63          BEQ  BR5
06DC:38         64          SEC             ;SET CARRY FLAG FOR SUBTRACTION
06DD:BD 80 0E   65          LDA  $0E80,X    ;FETCH DATA FROM FILE
06E0:ED 01 A0   66          SBC  $A001      ;SUBTRACT BACKGROUND (LOW 8 BITS)
06E3:9D 80 E0   67          STA  $E080,X    ;UPDATE FILE
06E6:BD 00 A0   68          LDA  $A000,X    ;READ HIGHEST BITS OF BACKGROUND
06E9:29 3F      69          AND  #$3F       ;CLEAN OFF THE TWO MSB'S
06EB:8D 7E 0E   70          STA  $0E7E      ;PUT IN TEMPORARY FILE
06EE:BD 00 0F   71          LDA  $0F00,X    ;FETCH DATA FROM FILE
06F1:ED 7E 0E   72          SBC  $0E7E      ;SUBTRACT TEMPORARY FILE
06F4:9D 00 0F   73          STA  $0F00,X    ;UPDATE FILE
06F7:BD 80 0F   74          LDA  $0F80,X    ;FETCH CARRY FILE
06FA:E9 00      75          SBC  #00        ;SUBTRACT CARRY IF STILL SET
06FC:9D 80 0F   76          STA  $0F80,X    ;UPDATE FILE
06FF:CA         77          DEX             ;DECREMENT THE DIODE COUNTER
0700:10 D3      78          BPL  BR5        ;READ ANOTHER DIODE ?
0702:88         79          DEY             ;DECREMENT REPLICATE COUNTER
0703:EA         80          NOP
0704:D0 B8      81          BNE  BR4        ;READ WHOLE ARRAY AGAIN ?
0706:60         82 FINISH   RTS             ;GO BACK TO BASIC PROGRAMME
```

The signal to noise ratio program SNR03 logs the data points for 32 diodes 32 times and stores each acquisition separately. This takes 2048 bytes of memory for storage (2 bytes per data point). It then calculates the mean, standard deviation and the ratio as the signal to noise ratio for each of the 32 diodes and prints them out. It then allows the subtraction from the individual data values of 32 values for 32 diodes for a selected background condition. It then recalculates the subtracted mean, standard deviation and signal to noise ratio and prints them out.

The diode numbers on the print out are for the position of the diode within those logged, not its position on the array.

The machine code program first converts the identity of the diodes to be logged into a series of numbers corresponding to the size of groups of diodes to be omitted or recorded. It makes extensive use of subroutines and indirect indexed addressing. It was this program in its background subtraction mode that set the limiting speed of data acquisition.

Getting this program and its data storage space into the 4k of RAM available on the AIM 65 was difficult.

```
10  REM  **AIM 65 PROGRAM**SNR03
20  REM SIGNAL/NOISE RATIO FOR A 128 DIODE ARRAY (WITH BACKGROUND SUBTRACTION)
30  REM  A TOTAL OF 32 DIODES IN UP TO 4 GROUPS ARE LOGGED 32 TIMES AND MEAN,STD

35  REM DEVIATION AND SIGNAL TO NOISE RATIO PRINTED OUT
40  REM *THE STARTING DIODE #'S  MUST BE IN NUMERICAL ORDER
50  DIM A(7): PRINT "1ST,#,4TIMES,MAX32": POKE 4,166: POKE 5,6:B = 2048
60  REM THE # OF THE 1ST DIODE IN A GROUP AND THE # OF DIODES IN THAT GROUP
70  REM  IS ENTERED(TOTAL DIODES 32 )
80 C = 2040:D = 32: INPUT A(0),A(1),A(2),A(3),A(4),A(5),A(6),A(7)
90 E =  SQR (31):F = 992:G = 3072:H = 256:AA = 16383:BB = H * H
100  FOR I = 0 TO 7: POKE C + I,A(I): NEXT I:J =  USR (K)
110  REM LOADS DIODE NUMBERS TO ADDRESSES $07F8 TO $07FF
120  IF  PEEK (2039) = 1 GOTO 150
130  REM THIS IS A M/C TEST FOR       INPUT ERROR
140  PRINT "INPUT WRONG": GOTO 50
150  FOR M = 0 TO 31:N = M + 1:O = 0:P = 0
160  FOR Q = 0 TO F STEP D:R = Q + M:S =  PEEK (B + R):T =  PEEK (G + R):U = T *
 H + S
170  IF AA < U THEN U =  - (BB - U)
175  REM THIS CORRECTS FOR VALUE BEING NEGATIVE AFTER THE SUBTRACTION
180 V = U * U:O = O + U:P = P + V: NEXT Q
190 X = O / D:Y =  SQR (P - O * O / D) / E: PRINT N;X / Y;X * 5 / (D * H);Y * 5
/ (D * H)
195  REM PRINTS OUT SNR,MEAN AND STD DEVIATION FOR EACH DIODE SELECTED
197  REM *CAUTION THE DIODE # IN THE PRINT OUT GIVES IT'S POSITION WITHIN THOSE
198  REM LOGGED.NOT IT'S POSITION ON THE ARRAY
200  NEXT M
210  IF  PEEK (2038) = 0 GOTO 260
220  POKE 2038,0
230  POKE 4,117: POKE 5,7
240 JJ =  USR (KK)
250  GOTO 150
260  PRINT "DONE ? Y=1,N=0": INPUT Z
270  IF Z = 0 THEN 50
280  STOP
```

```
SOURCE FILE: MSNR03
----- NEXT OBJECT FILE NAME IS MSNR03.OBJ0
0620:            1         ORG  $0620
0620:            2 *MACHINE LANGUAGE PROGRAM FOR AIM 65.
0620:            3 *TO COLLECT DATA FOR 32 DIODES 32 TIMES AND STORE ALL VALUES
0620:            4 *SEPARATELY.ALSO HAS BACKGROUND SUBTRACTION OPTION
0620:            5 *                            SUBROUTINE#1 COUNT UNLOGGED DIODES
0620:AD 0D A0    6 BR1     LDA  $A00D
0623:29 02       7         AND  #$02
0625:F0 F9       8         BEQ  BR1
0627:AD 01 A0    9         LDA  $A001
062A:60         10         RTS
062B:EA         11         NOP
062C:EA         12         NOP
062D:EA         13         NOP
062E:           14 *                            SUBROUTINE#2 LOG DATA VALUES
062E:AD 0D A0   15 BR2     LDA  $A00D
0631:29 02      16         AND  #$02
0633:F0 F9      17         BEQ  BR2
0635:AD 01 A0   18         LDA  $A001          ;READ VALUE LOW BYTE
0638:91 F0      19         STA  ($F0),Y
063A:AD 00 A0   20         LDA  $A000          ;READ VALUE HIGH BYTE
063D:29 3F      21         AND  #$3F           ;CLEAN OFF UNWANTED BITS
063F:91 F2      22         STA  ($F2),Y
0641:60         23         RTS
0642:EA         24         NOP
0643:EA         25         NOP
0644:EA         26         NOP
0645:           27 *                            SUBROUTINE#3 LOG AND SUBTRACT
0645:           28 *                            BACKGROUND VALUES
0645:AD 0D A0   29 BR3     LDA  $A00D
0648:29 02      30         AND  #$02
064A:F0 F9      31         BEQ  BR3
064C:38         32         SEC
064D:B1 F0      33         LDA  ($F0),Y
064F:ED 01 A0   34         SBC  $A001
0652:91 F0      35         STA  ($F0),Y
0654:AD 00 A0   36         LDA  $A000
0657:29 03      37         AND  #3F
0659:8D F5 07   38         STA  $07F5
065C:B1 F2      39         LDA  ($F2),Y
065E:ED F5 07   40         SBC  $07F5
0661:91 F2      41         STA  ($F2),Y
0663:60         42         RTS
0664:EA         43         NOP
0665:EA         44         NOP
0666:EA         45         NOP
0667:           46 *                            SUBROUTINE#4 ADD $20 TO ADDRESSES IN
0667:           47 *                            $F0/F1 AND $F2/F3 FOR NEXT CYCLE
0667:D8         48 BR5     CLD
0668:18         49         CLC
0669:A5 F0      50         LDA  $F0
066B:69 20      51         ADC  #$20
066D:85 F0      52         STA  $F0
066F:A5 F1      53         LDA  $F1
0671:69 00      54         ADC  #$00
0673:85 F1      55         STA  $F1
0675:18         56         CLC
0676:A5 F2      57         LDA  $F2
0678:69 20      58         ADC  #$20
```

```
067A:85 F2       59           STA  $F2
067C:A5 F3       60           LDA  $F3
067E:69 00       61           ADC  #$00
0680:85 F3       62           STA  $F3
0682:CA          63           DEX
0683:60          64           RTS
0684:EA          65           NOP
0685:EA          66           NOP
0686:EA          67           NOP
0687:            68 *                        SUBROUTINE#5 SET UP BASE ADDRESSES
0687:A2 20       69 BR6       LDX  #$20      ;SET FOR 32 CYCLES
0689:A9 00       70           LDA  #$00
068B:85 F0       71           STA  $F0
068D:85 F2       72           STA  $F2
068F:A9 08       73           LDA  #$08      ;LOW BYTE BASE ADDRESS $0800
0691:85 F1       74           STA  $F1
0693:A9 0C       75           LDA  #$0C      ;HIGH BYTE BASE ADDRESS $0C00
0695:85 F3       76           STA  $F3
0697:A9 00       77           LDA  #$00
0699:8D 0C A0    78           STA  $A00C     ;SET PCR FOR INTERRUPT ON A 1 TO 0
069C:            79 *                        TRANSITION
069C:8D 02 A0    80           STA  $A002     ;SET ORA AND ORB AS INPUTS
069F:8D 03 A0    81           STA  $A003
06A2:60          82           RTS
06A3:EA          83           NOP
06A4:EA          84           NOP
06A5:EA          85           NOP
06A6:D8          86           CLD            ;ENTRY POINT INTO THE PROGRAM FROM BAS
IC
06A7:78          87           SEI
06A8:AD FE 07    88           LDA  $07FE     ;THIS PART OF THE PROGRAM TESTS FOR
06AB:38          89           SEC            ;ERRORS IN INPUT BY ENSURING THAT NO
06AC:ED FD 07    90           SBC  $07FD     ;DIODE BELONGS TO MORE THAN ONE GROUP
06AF:38          91           SEC            ;THAT IS TO BE LOGGED
06B0:ED FC 07    92           SBC  $07FC
06B3:8D FE 07    93           STA  $07FE     ;THIS IS THE # OF DIODES TO BE IGNORED
06B6:90 2B       94           BCC  BR4       ;BETWEEN THE 3RD AND 4TH GROUPS TO BE
06B8:            95 *                        LOGGED.BR4 IS THE ERROR BRANCH
06B8:AD FC 07    96           LDA  $07FC
06BB:38          97           SEC
06BC:ED FB 07    98           SBC  $07FB
06BF:38          99           SEC
06C0:ED FA 07   100           SBC  $07FA
06C3:8D FC 07   101           STA  $07FC     ;THIS IS THE # OF DIODES TO BE IGNORED
06C6:90 1B      102           BCC  BR4       ;BETWEEN THE 2ND AND 3RD GROUPS TO BE
06C8:           103 *                        LOGGED
06C8:AD FA 07   104           LDA  $07FA
06CB:38         105           SEC
06CC:ED F9 07   106           SBC  $07F9
06CF:38         107           SEC
06D0:ED F8 07   108           SBC  $07F8
06D3:8D FA 07   109           STA  $07FA     ;THIS IS THE # OF DIODES TO BE IGNORED
06D6:90 0B      110           BCC  BR4       ;BETWEEN THE 1ST AND 2ND GROUPS TO BE
06D8:           111 *                        LOGGED
06D8:A9 01      112           LDA  #$01
06DA:8D F7 07   113           STA  $07F7     ;THIS THE SIGNAL FOR ERROR FREE INPUT
06DD:8D F6 07   114           STA  $07F6     ;THIS IS THE SIGNAL FOR THE ANALYTE
06E0:           115 *                        DATA COLLECTION CYCLE
06E0:4C EB 06   116           JMP  NOERROR
06E3:A9 00      117 BR4       LDA  #$00
06E5:8D F7 07   118           STA  $07F7     ;THIS IS THE SIGNAL FOR INPUT ERROR
```

```
06E8:4C EB 07   119          JMP  FINISH    ;GO BACK TO BASIC PROGRAM AND RE-ENTER
                                                     INPUT
06EB:           120 *
06EB:18         121 NOERROR CLC
06EC:EA         122          NOP
06ED:EA         123          NOP
06EE:EA         124          NOP
06EF:AD F9 07   125          LDA  $07F9     ;THIS SECTION ADDS AND STORES DIODE
06F2:6D FB 07   126          ADC  $07FB     ;GROUP TOTALS
06F5:8D FB 07   127          STA  $07FB
06F8:6D FD 07   128          ADC  $07FD
06FB:8D FD 07   129          STA  $07FD
06FE:6D FF 07   130          ADC  $07FF
0701:8D FF 07   131          STA  $07FF
0704:CE F8 07   132          DEC  $07F8     ;THIS GIVES THE # OF THE LAST DIODE
0707:           133 *                        TO BE IGNORED AT THE START OF THE
0707:           134 *                        ARRAY SCAN
0707:20 B7 06   135          JSR  BR6
070A:AD 00 A0   136 BR18     LDA  $A000     ;CLEAR IFR
070D:AD 0D A0   137 BR7      LDA  $A00D     ;LOOK FOR START PULSE
0710:29 10      138          AND  #$10
0712:F0 F9      139          BEQ  BR7       ;NOT FOUND IT YET ?
0714:AD 00 A0   140          LDA  $A000     ;CLEAR IFR
0717:AC F8 07   141          LDY  $07F8     ;LOAD # OF LAST DIODE TO BE IGNORED AT
071A:           142 *                        START OF SCAN
071A:F0 08      143          BEQ  BR10      ;IF 0 START LOGGING DATA
071C:20 20 06   144 BR9      JSR  BR1       ;COUNT OF 1ST SET OF UNWANTED DIODES
071F:88         145          DEY
0720:D0 FA      146          BNE  BR9
0722:A0 00      147          LDY  #$00      ;ZERO COUNTER FOR 1ST SET OF LOGGED
0724:           148 *                        DIODES
0724:20 2E 06   149 BR10     JSR  BR2       ;LOG A DIODE VALUE
0727:C8         150          INY            ;COUNT IT
0728:CC F9 07   151          CPY  $07F9     ;ARE THEY ALL DONE ?
072B:90 F7      152          BCC  BR10      ;IF NOT LOG ANOTHER ONE
072D:AC FA 07   153          LDY  $07FA     ;LOAD COUNTER WITH # OF DIODES TO BE
0730:           154 *                        IGNORED
0730:20 20 06   155 BR11     JSR  BR1       ;COUNT OF 2ND SET OF UNWANTED DIODES
0733:88         156          DEY
0734:D0 FA      157          BNE  BR11
0736:AC F9 07   158          LDY  $07F9     ;START THE COUNTER HERE FOR THE 2ND
0739:           159 *                        GROUP OF DIODES TO BE LOGGED
0739:20 2E 06   160 BR12     JSR  BR2       ;LOG A DIODE VALUE (2ND SET)
073C:C8         161          INY            ;COUNT IT
073D:CC FB 07   162          CPY  $07FB     ;DONE ?
0740:90 F7      163          BCC  BR12      ;IF NOT LOG ANOTHER
0742:AC FC 07   164          LDY  $07FC     ;LOAD COUNTER WITH # OF DIODES TO BE
0745:           165 *                        IGNORED
0745:20 20 06   166 BR13     JSR  BR1       ;COUNT UNWANTED DIODES
0748:88         167          DEY
0749:D0 FA      168          BNE  BR13
074B:AC FB 07   169          LDY  $07FB     ;START COUNTER HERE FOR 3RD GROUP OF
074E:           170 *                        DIODES TO BE LOGGED
074E:20 2E 06   171 BR14     JSR  BR2       ;LOG A DIODE VALUE (3RD SET)
0751:C8         172          INY            ;COUNT IT
0752:CC FD 07   173          CPY  $07FD     ;DONE ?
0755:90 F7      174          BCC  BR14      ;IF NOT LOG ANOTHER
0757:AC FE 07   175          LDY  $07FE     ;LOAD COUNTER WITH # OF DIODES TO BE
075A:           176 *                        IGNORED
075A:20 20 06   177 BR15     JSR  BR1       ;COUNT UNWANTED DIODES
075D:88         178          DEY
```

```
075E:D0 FA      179            BNE  BR15
0760:AC FD 07   180            LDY  $07FD     ;START COUNTER HERE FOR 4TH GROUP OF
                                               DIODES TO BE LOGGED
0763:           181 *
0763:20 2E 06   182 BR16       JSR  BR2       ;LOG A DIODE VALUE (4TH SET)
0766:C8         183            INY            ;COUNT IT
0767:CC FF 07   184            CPY  $07FF     ;DONE ?
076A:90 F7      185            BCC  BR16      ;IF NOT LOG ANOTHER
076C:20 67 06   186            JSR  BR5       ;CHANGE ADDRESSES OF THE DATA STORAGE
                                               REGISTERS FOR THE NEXT SET OF DATA
076F:           187 *
076F:F0 03      188            BEQ  BR17      ;IF ANALYTE DATA COLLECTION COMPLETE
0771:           189 *                          STOP AND GO BACK TO BASIC TO SET UP
0771:           190 *                          FOR BACKGROUND DATA COLLECTION
0771:4C 0A 07   191            JMP  BR18      ;IF LESS THAN 32 SCANS GO ROUND AGAIN
0774:60         192 BR17       RTS
0775:00         193            BRK            ;THIS IS THE ENTRY POINT FROM BASIC
0776:           194 *                          FOR THE BACKGROUND SUBTRACTION
0776:EA         195            NOP
0777:EA         196            NOP
0778:20 87 06   197            JSR  BR6       ;INITIALISE FOR BACKGROUND SUBTRACTION
077B:AD 00 A0   198 BR19       LDA  $A000     ;CLEAR IFR
077E:AD 0D A0   199 BR20       LDA  $A00D     ;LOOK FOR START PULSE
0781:29 10      200            AND  #$10      ;ON CONTROL LINE CB1
0783:F0 F9      201            BEQ  BR20      ;CAN'T FIND IT KEEP LOOKING
0785:AD 00 A0   202            LDA  $A000     ;CLEAR IFR
0788:AC FB 07   203            LDY  $07FB     ;LOAD # OF LAST DIODE TO BE IGNORED AT
078B:           204 *                          THE START OF THE SCAN
078B:F0 08      205            BEQ  BR23      ;IF 0 START LOGGING DATA
078D:20 20 06   206 BR22       JSR  BR1       ;COUNT OF 1ST SET OF UNWANTED DIODES
0790:88         207            DEY
0791:D0 FA      208            BNE  BR22
0793:A0 00      209            LDY  #$00      ;ZERO COUNTER FOR 1ST SET OF LOGGED
0795:           210 *                          DIODES
0795:20 45 06   211 BR23       JSR  BR3       ;LOG AND SUBTRACT BACKGROUND DATA
0798:C8         212            INY            ;COUNT
0799:CC F9 07   213            CPY  $07F9     ;DONE ?
079C:90 F7      214            BCC  BR23      ;IF NOT DO IT AGAIN
079E:AC FA 07   215            LDY  $07FA     ;LOAD COUNTER WITH # OF DIODES TO BE
07A1:           216 *                          IGNORED
07A1:20 20 06   217 BR24       JSR  BR1       ;COUNT UNWANTED DIODES
07A4:88         218            DEY
07A5:D0 FA      219            BNE  BR24
07A7:AC F9 07   220            LDY  $07F9     ;START THE COUNTER HERE FOR THE 2ND
07AA:           221 *                          GROUP OF DIODES TO BE LOGGED
07AA:20 45 06   222 BR25       JSR  BR3       ;LOG AND SUBTRACT BACKGROUND DATA-
07AD:C8         223            INY            ;(2ND SET)
07AE:CC FB 07   224            CPY  $07FB
07B1:90 F7      225            BCC  BR25
07B3:AC FC 07   226            LDY  $07FC     ;LOAD WITH # OF DIODES TO BE IGNORED
07B6:20 20 06   227 BR26       JSR  BR1       ;COUNT UNWANTED DIODES
07B9:88         228            DEY
07BA:D0 FA      229            BNE  BR26
07BC:AC FB 07   230            LDY  $07FB     ;START COUNTER FOR 3RD GROUP OF
07BF:           231 *                          DIODES TO BE LOGGED
07BF:20 45 06   232 BR27       JSR  BR3       ;LOG AND SUBTRACT BACKGROUND DATA
07C2:C8         233            INY            ;3RD SET
07C3:CC FD 07   234            CPY  $07FD     ;DONE ?
07C6:90 F7      235            BCC  BR27      ;IF NOT LOG AGAIN
07C8:AC FE 07   236            LDY  $07FE     ;LOAD COUNTER WITH 4TH GROUP OF
07CB:           237 *                          DIODES TO BE IGNORED
07CB:20 20 06   238 BR28       JSR  BR1       ;COUNT UNWANTED DIODES
```

```
07CE:88         239          DEY
07CF:D0 FA      240          BNE  BR28
07D1:AC FD 07   241          LDY  $07FD      ;START COUNTER HERE FOR 4TH SET OF
07D4:           242 *                         LOGGED DIODES
07D4:20 45 06   243 BR29     JSR  BR3        ;LOG AND SUBTRACT SET #4
07D7:C8         244          INY
07D8:CC FF 07   245          CPY  $07FF
07DB:90 F7      246          BCC  BR29
07DD:EA         247          NOP
07DE:EA         248          NOP
07DF:EA         249          NOP
07E0:EA         250          NOP
07E1:EA         251          NOP
07E2:EA         252          NOP
07E3:20 67 06   253          JSR  BR5        ;CHANGE ADDRESSES OF THE DATA STORAGE
07E6:           254 *                         REGISTERS FOR THE NEXT SET OF DATA
07E6:F0 03      255          BEQ  FINISH     ;IF DONE GO BACK TO BASIC
07E8:4C 7B 07   256          JMP  BR19       ;IF NOT DONE LOOK FOR ANOTHER
07EB:           257 *                         START PULSE
07EB:60         258 FINISH   RTS
```

APPENDIX 5

APPENDIX 5

SCRATCHPAD MEMORY USAGE WITH THE APPLE II+

ADDRESS		
HEXADECIMAL	DECIMAL	USAGE BY THE INPUT BUFFER
7F01	32,513	8253 #3 COUNTER #0 LOW BYTE
7F02		8253 #3 COUNTER #0 HIGH BYTE
7F03		8253 #3 COUNTER #1 LOW BYTE
7404		8253 #3 COUNTER #1 HIGH BYTE
7F05		8253 #3 COUNTER #2 LOW BYTE
7F06		8253 #3 COUNTER #2 HIGH BYTE
7F07		8353 #4 COUNTER #0 LOW BYTE
7F08		8253 #4 COUNTER #0 HIGH BYTE
7F09		8253 #4 COUNTER #1 LOW BYTE
7F0A		8253 #4 COUNTER #1 HIGH BYTE
7F0B		8253 #4 COUNTER #2 LOW BYTE
7F0C		8253 #4 COUNTER #2 HIGH BYTE
7F0D	32,525	GAIN CODE ARRAY #0
7F0E		GAIN CODE ARRAY #1
7F0F		GAIN CODE ARRAY #2
7F10		GAIN CODE ARRAY #3
7F11		GAIN CODE ARRAY #4
7F12		GAIN CODE ARRAY #5
7F13	32,531	# OF REPLICATES ARRAY #0
7F14		# OF REPLICATES ARRAY #1
7F15		# OF REPLICATES ARRAY #2
7F16		# OF REPLICATES ARRAY #3
7F17		# OF REPLICATES ARRAY #4
7F18		# OF REPLICATES ARRAY #5
7F19	32,537	
7F1A		
7F1B		# OF REPLICATES, DUPLICATE
7F1C		LIST, TO BE DECREMENTED
7FAD		
7F1E		
7F1F	32,543	TEMPORARY ADDRESS ARRAY IDENTITY CODE
7F20		
7F21		
7F22		
7F23		
7F24	32,548	GAIN AND CHANNEL CODE FOR SELECTED ARRAY

ADDRESS		
HEXADECIMAL	DECIMAL	USAGE
7F25		
		USAGE BY BACKGROUND RAW DATA FILE
7F26	32,550	
7F27		
7F28		
7F29		
7F2A		
7F2B		8253 DATA SPECIFYING INTEGRATION TIMES FOR THE BACKGROUND RAW DATA FILE
7F2C		
7F2D		
7F2E		
7F2F		
7F30		
7F31		
7F32	32,562	
7F33		
7F34		GAIN CODES FOR BACKGROUND RAW DATA FILE
7F35		
7F36		
7F37		
7F38	32,568	
7F39		
7F3A		# OF REPLICATES FOR BACKGROUND RAW DATA FILE
7F3B		
7F3C		
7F3D		
7F3E	32,574	USAGE BY ANALYTE MEANS FILE
7F3F		
7F40		
7F41		
7F42		
7F43		8253 DATA SPECIFYING INTEGRATION TIMES FOR THE ANALYTE MEANS FILE
7F44		
7F45		
7F46		
7F47		
7F48		
7F49		
7F4A	32,586	
7F4B		
7F4C		GAIN CODES FOR ANALYTE MEANS FILE
7F4D		
7F4E		
7F4F		
7F50	32,592	
7F51		

ADDRESS			
HEXADECIMAL	DECIMAL		
7F52		# OF REPLICATES FOR ANALYTE MEANS FILE	
7F53			
7F54			
7F55			
7F56	32,598	USAGE BY BACKGROUND MEANS FILE	
7F47			
7F58			
7F59			
7F5A			
7F5B		8253 DATA SPECIFYING INTEGRATION TIMES FOR THE BACKGROUND MEANS FILE	
7F5C			
7F5D			
7F5E			
7F5F			
7F60			
7F61			
7F62	32,610		
7F63			
7F64		GAIN CODES FOR BACKGROUND MEANS FILE	
7F65			
7F66			
7F67			
7F68	32,616		
7F69			
7F6A		# OF REPLICATES FOR BACKGROUND MEANS FILE	
7F6B			
7F6C			
7F6D			
7F6E	32,622	ADDRESS LOW BYTE	LOW BYTE ADDRESS FOR DAC DISPLAYS
7F6F	32,623	ADDRESS HIGH BYTE	
7F70	32,624	ADDRESS LOW BYTE	HIGH BYTE ADDRESS FOR DAC DISPLAYS
7F71	32,625	ADDRESS HIGH BYTE	
7F72	32,626	INNER LOOP CMP ADDRESS FOR RECORDER	
7F73	32,627	DELAY VALUE FOR CHART RECORDER	
7F74	32,628	OFFSET VALUE FOR RECORDER OUTPUT	

APPENDIX 6

APPENDIX 6

APPLE II+ PROGRAMS

The 6 array system programs are menu driven and user friendly. DRA is the display program that runs when the system is booted and its main purpose is to make sure that the disks are in their correct drives.

DRS is the main menu program.

SEL1 receives integration time information and stores it in scratchpad memory. It corrects the values of the integration times so that they follow the rules that avoid readout clashes. It then calls its own machine code program MC1BA.OBJ0.

The machine code program closes the gates on the counters on the first two 8253 chips by generating a low logic level through the game I/O port. It checks again, this time in machine code, that the integration times follow the readout clash avoidance rules. It loads all the counters and then opens the gates so that the timing operations can commence. The program then calls the next option, SEL2.

```
]LIST

5  REM PROGRAM**DRA**
10  HIMEM: 29439
20  REM INITIAL DISPLAY WHEN SYSTEM BOOTED
30  HOME
40  HTAB 8: PRINT "DIRECT READER DATA HANDLING"
50  HTAB 16: PRINT "PROGRAMS"
60  PRINT : PRINT "THE SYSTEM DISC SHOULD BE IN DRIVE #1": PRINT : PRINT
70  PRINT "FILE DISCS SHOULD BE IN DRIVE #2"
80  PRINT : FOR X = 1 TO 2000: NEXT X: PRINT
90  PRINT "****************************************"
100  PRINT : PRINT "DATA IS COLLECTED AND MANIPULATED IN": PRINT : PRINT
110  PRINT "BINARY AND CONVERTED TO VOLTAGE"
120  FOR X = 1 TO 4000: NEXT X: PRINT : PRINT
130  PRINT "SELECT ONE OF THE FOLLOWING OPTIONS BY"
140  PRINT "ENTERING THE NUMBER": PRINT : PRINT
150  PRINT  CHR$ (4);"RUNDRS"
```

```
5  REM  PROGRAM **DRS**
10  HIMEM: 29439
15  REM PROGRAM FOR SELECTION OF OPTIONS
20  HTAB 4: PRINT "1. DEFINE THE INTEGRATION TIMES"
30  HTAB 4: PRINT "2. ACQUIRE SETS OF DATA POINTS"
40  HTAB 4: PRINT "3. SET UP A SHORT INTEGRATION TIME"
50  HTAB 9: PRINT "FOR A SINGLE ARRAY"
60  HTAB 4: PRINT "4. SUBTRACT BACKGROUND AND"
70  HTAB 9: PRINT "STORE AS MEANS"
80  HTAB 4: PRINT "5. DISPLAY GRAPHICALLY ON THIS SCREEN"
90  HTAB 4: PRINT "6. SAVE DATA ON DISKETTE"
100  HTAB 4: PRINT "7. DISPLAY ON AN OSCILLOSCOPE"
110  HTAB 4: PRINT "8. OUTPUT TO CHART RECORDER"
120  HTAB 4: PRINT "9. DISPLAY VALUES ON THIS SCREEN"
130  HTAB 4: PRINT "10. SMOOTH (PAIR AVERAGE) THE"
140  HTAB 9: PRINT "INPUT BUFFER"
150  HTAB 4: PRINT "11. OBTAIN DATA VALUES FROM A FILE"
160  HTAB 4: PRINT "12. CALCULATE CONCENTRATIONS": PRINT
170  PRINT "ENTER INSTRUCTION # AND PRESS RETURN"
180  INPUT B$
185 D$ =  CHR$ (13) +  CHR$ (4)
190  ON  VAL (B$) GOTO 210,220,230,240,250,260,270,280,290,300,310,330
200  IF  VAL (B$) > 12 GOTO 10
210  PRINT D$;"RUNSEL1"
220  PRINT D$;"RUNSEL2"
230  PRINT D$;"RUNSEL3"
240  PRINT D$;"RUNSEL4"
250  PRINT D$;"RUNSEL5"
260  PRINT D$;"RUNSEL6"
270  PRINT D$;"RUNSEL7"
280  PRINT D$;"RUNSEL8"
290  PRINT D$;"RUNSEL9"
300  PRINT D$;"RUNSEL10"
310  PRINT D$;"RUNSEL11"
330  PRINT D$;"RUNSEL12"
```

```
5  REM PROGRAM  **SEL1**
10  HIMEM: 29439
15  REM  PROGRAM TO SET THE INTEGRATION TIMES FOR SIX ARRAYS
20  HOME
30  PRINT "IF NEW INTEGRATION TIMES ENTER 1"
40  PRINT
50  PRINT "IF SAME AS BEFORE ENTER 2"
60  INPUT P$
70  ON  VAL (P$) GOTO 90,310
90  PRINT
100  PRINT "ENTER INTEGRATION TIMES IN SECONDS FOR  SIX ARRAYS(MAXIMUM 205 SECS)
110  PRINT "IF ARRAY NOT USED ENTER 0"
120  FOR I = 0 TO 5:
125  REM FOR EACH ARRAY
130  PRINT "ARRAY #  ";I: INPUT B
140 E = 0.5:F = 256:D = 3.1289E - 3:H = 32
150  IF B = 0 THEN 230
155  REM ROUND OFF INTEGRATION TIME TO AN INTEGER MULTIPLE
156  REM OF THE STANDARD TIME INCREMENT
160 C =  INT (B / (D * H) + E) * H
165  REM  DIVIDE INTO A TWO BYTE VALUE AND POKE INTO SCRATCH PAD MEMORY
170 T = C / F:G =  INT (T)
180 J =  INT (F * (T - G) + E)
190  IF G > 255 THEN  PRINT "TOO LONG": GOTO 130
200  IF G > 0 THEN 240
210  IF J < 32 THEN  PRINT "TOO SHORT": GOTO 320
220  GOTO 240
230 G = 0:J = H:C = H
240  POKE 32513 + 2 * I,J: POKE 32514 + 2 * I,G
250 L = C * D
260 L =  INT (L * 10 ^ 4 + .5) /  INT (10 ^ 4 + .5)
270  PRINT  CHR$ (4);"PR#1"
280  PRINT "ACTUAL INTEGRATION TIME ARRAY# ";I;"=";L;"SECONDS"
290  PRINT  CHR$ (4);"PR#0"
300  NEXT I
305  REM RUN THE MACHINE CODE PROGRAM THAT LOADS THE 8253 COUNTERS
310  PRINT  CHR$ (4);"BRUNMC1BA.OBJ0"
315  REM NOW COLLECT DATA
320  PRINT  CHR$ (4);"RUNSEL2"
```

```
SOURCE FILE: MC1BA
0000:              1 ****MC1BA****
0000:              2 *PART OF PROGRAM FOR SETTING INTEGRATION TIMES FOR 6 ARRAYS
0000:              3 *THE BASIC PROGRAM HAS PREVIOUSLY POKED THE INTEGRATION TIMES
 INTO SCRATCH PAD MEMORY
----- NEXT OBJECT FILE NAME IS MC1BA.OBJ0
9237:              4          ORG  $9237
9237:              5 *CLOSE THE GATE ON 8253 #1 COUNTER 0 DURING LOADING
9237:AD 58 C0      6          LDA  $C058
C0D0:              7 CLK      EQU  $C0D0
923A:              8 *FOR 8253 # 1
923A:A9 34         9          LDA  #$34       ;LOAD MODE WORD COUNTER 0 MODE 2
923C:8D D3 C0     10          STA  CLK+3      ;LOAD INTO 8253 #1
923F:A9 50        11          LDA  #$50       ;LOAD MODE WORD COUNTER 1 MODE 0
9241:8D D3 C0     12          STA  CLK+3      ;LOAD INTO 8253 #1
9244:A9 90        13          LDA  #$90       ;LOAD MODE WORD COUNTER " MODE 2
9246:8D D3 C0     14          STA  CLK+3      ;LOAD INTO 8253 #1
9249:             15 *COUNTER #0 IN MODE 2 DIVIDES CLOCK RATE BY 3200
9249:A9 80        16          LDA  #$80       ;LOAD COUNTER 0 LOW BYTE
924B:8D D0 C0     17          STA  CLK        ;WRITE LOW BYTE
924E:A9 0C        18          LDA  #$0C       ;LOAD COUNTER 0 HIGH BYTE
9250:8D D0 C0     19          STA  CLK        ;WRITE HIGH BYTE
9253:             20 *COUNTERS #1 AND 2 OF 8253 #1 AND ALL 3 COUNTERS OF 8253 #2
9253:             21 *ARE IN MODE 0.THEY GATE COUNTERS #1 AND 2 OF 8253 #3 AND
9253:             22 *ALL 3 COUNTERS OF 8253 #4 THEREBY DELAYING THE START OF
9253:             23 *THEIR COUNTS
9253:A9 04        24          LDA  #$04       ;LOAD COUNTER 1 LOW BYTE (ONLY)
9255:8D D1 C0     25          STA  CLK+1      ;WRITE LOW BYTE (ONLY)
9258:A9 09        26          LDA  #$09       ;LOAD COUNTER 2 LOW BYTE (ONLY)
925A:8D D2 C0     27          STA  CLK+2      ;WRITE LOW BYTE (ONLY)
925D:             28 *FOR 8253 # 2
925D:A9 10        29          LDA  #$10       ;LOAD MODE WORD COUNTER 0 MODE 0
925F:8D D7 C0     30          STA  CLK+7      ;LOAD INTO 8253 #2
9262:A9 50        31          LDA  #$50       ;LOAD MODE WORD COUNTER 1 MODE 0
9264:8D D7 C0     32          STA  CLK+7      ;LOAD INTO 8253 #2
9267:A9 90        33          LDA  #$90       ;LOAD MODE WORD COUNTER 2 MODE 0
9269:8D D7 C0     34          STA  CLK+7      ;LOAD INTO 8253 #2
926C:A9 0F        35          LDA  #$0F       ;LOAD COUNTER 0 LOW BYTE (ONLY)
926E:8D D4 C0     36          STA  CLK+4      ;WRITE LOW BYTE (ONLY)
9271:A9 14        37          LDA  #$14       ;LOAD COUNTER 1 LOW BYTE (ONLY)
9273:8D D5 C0     38          STA  CLK+5      ;WRITE LOW BYTE (ONLY)
9276:A9 19        39          LDA  #$19       ;LOAD COUNTER 2 LOW BYTE (ONLY)
9278:8D D6 C0     40          STA  CLK+6      ;WRITE LOW BYTE (ONLY)
927B:             41 *8253'S #3 AND 4 CONTROL THE ACTUAL INTEGRATION TIMES.
927B:             42 *AFTER MODE WORDS ARE LOADED (ALL COUNTERS IN MODE 2)
927B:             43 *THE COUNTERS ARE LOADED WITH THEIR COUNTS FROM SCRATCH
927B:             44 *PAD MEMORY,WHERE THEY WERE PLACED BY THE BASIC PROGRAM
927B:A9 34        45          LDA  #$34       ;LOAD MODE WORD COUNTER 0 MODE 2
927D:8D DB C0     46          STA  CLK+$B     ;LOAD INTO 8253 #3
9280:A9 74        47          LDA  #$74       ;LOAD MODE WORD COUNTER 1 MODE 2
9282:8D DB C0     48          STA  CLK+$B     ;LOAD INTO 8253 #3
9285:A9 B4        49          LDA  #$B4       ;LOAD MODE WORD COUNTER 2 MODE 2
9287:8D DB C0     50          STA  CLK+$B     ;LOAD INTO 8253 #3
928A:AD 01 7F     51          LDA  $7F01      ;FETCH LOW BYTE 1ST INTEGRATION TIME
928D:29 E0        52          AND  #$E0       ;MAKE SURE IT IS A MULTIPLE OF 32
928F:8D D8 C0     53          STA  CLK+8      ;WRITE LOW BYTE
9292:AD 02 7F     54          LDA  $7F02      ;FETCH HIGH BYTE 1ST INTEGRATION TIME
9295:8D D8 C0     55          STA  CLK+8      ;WRITE HIGH BYTE
9298:AD 03 7F     56          LDA  $7F03      ;FETCH LOW BYTE 2ND INTEGRATION TIME
929B:29 E0        57          AND  #$E0       ;GUARANTEE THAT IT IS A MULTIPLE OF 32
929D:8D D9 C0     58          STA  CLK+9      ;WRITE LOW BYTE
```

```
92A0:AD 04 7F          LDA  $7F04      ;FETCH HIGH BYTE 2ND INTEGRATION TIME
92A3:8D D9 C0          STA  CLK+9      ;WRITE HIGH BYTE
92A6:AD 05 7F          LDA  $7F05      ;FETCH LOW BYTE 3RD INTEGRATION TIME
92A9:29 E0             AND  #$E0       ;A MULTIPLE OF 32 ?
92AB:8D DA C0          STA  CLK+$A     ;WRITE LOW BYTE
92AE:AD 06 7F          LDA  $7F06      ;FETCH HIGH BYTE 3RD INTEGRATION TIME
92B1:8D DA C0          STA  CLK+$A     ;WRITE HIGH BYTE
92B4:A9 34             LDA  #$34       ;LOAD MODE WORD COUNTER 0 MODE 2
92B6:8D DF C0          STA  CLK+$F     ;LOAD INTO 8253 #4
92B9:A9 74             LDA  #$74       ;LOAD MODE WORD COUNTER 0 MODE2
92BB:8D DF C0          STA  CLK+$F     ;LOAD INTO 8253 #4
92BE:A9 B4             LDA  #$B4       ;LOAD MODE WORD COUNTER 0 MODE 2
92C0:8D DF C0          STA  CLK+$F     ;LOAD INTO 8253 #4
92C3:AD 07 7F          LDA  $7F07      ;FETCH LOW BYTE 4TH INTEGRATION TIME
92C6:29 E0             AND  #$E0       ;A MULTIPLE OF 32 ?
92C8:8D DC C0          STA  CLK+$C     ;WRITE LOW BYTE
92CB:AD 08 7F          LDA  $7F08      ;FETCH HIGH BYTE 4TH INTEGRATION TIME
92CE:8D DC C0          STA  CLK+$C     ;WRITE HIGH BYTE
92D1:AD 09 7F          LDA  $7F09      ;FETCH LOW BYTE 5TH INTEGRATION TIME
92D4:29 E0             AND  #$E0       ;A MULTIPLE OF 32 ?
92D6:8D DD C0          STA  CLK+$D     ;WRITE LOW BYTE
92D9:AD 0A 7F          LDA  $7F0A      ;FETCH HIGH BYTE 5TH INTEGRATION TIME
92DC:8D DD C0          STA  CLK+$D     ;WRITE HIGH BYTE
92DF:AD 0B 7F          LDA  $7F0B      ;FETCH LOW BYTE 6TH INTEGRATION TIME
92E2:29 E0             AND  #$E0       ;A MULTIPLE OF 32 ?
92E4:8D DE C0          STA  CLK+$E     ;WRITE LOW BYTE
92E7:AD 0C 7F          LDA  $7F0C      ;FETCH HIGH BYTE 6TH INTEGRATION TIME
92EA:8D DE C0          STA  CLK+$E     ;WRITE HIGH BYTE
92ED:EA                NOP
92EE:EA                NOP
92EF:EA                NOP
92F0:          *ALL COUNTERS LOADED SO OPEN THE GATE ON 8253 #1 COUNTER 0
92F0:AD 59 C0          LDA  $C059
92F3:60                RTS             ;GO AND DO SOMETHING ELSE
```

The program SEL2 is the data acquisition program. It has provisions for signal averaging but not background subtraction which is handled separately. The BASIC program asks for, and POKES into scratchpad memory, the range setting for the programmable AI13 analog to digital converter and the number of replications required for each array. It then calls the machine code program MC2AA.OBJ0 to get the data values and later calls other programs to transfer the data to other memory locations (files) before or after calculation of mean values.

The machine language program MC2AA is relatively complex. It first makes a second copy of the replications requested, the second set to be decremented as counters. It looks for the rising edge of a start pulse and identifies the array about to be read out. It then checks if the array data set is needed and if it is, it selects the gain code for that array from scratch pad memory and sets the A/DC to the required range and channel. The program then generates the base addresses for the low, high and carry bytes of data for that array, (indexing is used to differentiate between the diodes) and writes them forward in the program. It then looks for the falling edge of the start pulse and commences the data acquisition loop for that array. It cues the A/DC to convert on receipt of a trigger and polls for a conversion completed signal. The A/DC output values are read and stored in the appropriate addresses.

After each array has been logged, the replicate count for that array is decremented. When all replicate counts have been decremented to zero the program ends.

Other programs called by SEL2 are:-

i. MC2B.OBJ0 which transfers the new data to the Background Raw Data File using machine code.

ii. SEL2A which calculates the mean values and stores them in the Analyte Means File; MC5 is used to transfer the replication and gain parameters in machine code.

iii. SEL2B and MC6 which perform the same function, transferring to the Background Means File.

```
5  REM PROGRAM **SEL2**
10  HIMEM: 29439
15  REM THIS IS THE DATA ACQUISITION PROGRAM
20  HOME
30  HTAB 5: PRINT "ACQUISITION OF DATA POINTS": PRINT : PRINT
40  HTAB 5: PRINT "TWO PARAMETERS ARE REQUIRED"
50  PRINT : PRINT : PRINT ;"1. THE CONVERSION RANGE OF THE ADC": PRINT : PRINT
60  PRINT "2.THE NUMBER OF REPLICATES FOR EACH        ARRAY"
70  PRINT : PRINT : PRINT ;"IF NEW PARAMETERS ENTER 1": PRINT
75  PRINT "IF THE SAME ENTER 2 "
80  INPUT M
90  IF M = 1 THEN 110
100  IF M = 2 THEN 400
110  FOR I = 0 TO 5
120 D$ =  CHR$ (4)
130  PRINT D$;"PR#1"
140  PRINT "ARRAY #";I
150  PRINT D$;"PR#0"
160  PRINT "SELECT THE # CORRESPONDING TO THE        EXPECTED SIGNAL RANGE"
165  REM  SET THE A/DC RANGE
170  PRINT "0. 0 TO +5.0VOLTS"
180  PRINT "1  0 TO +1.0VOLTS"
190  PRINT "2  0 TO +0.5VOLTS"
200  PRINT "3  0 TO +0.1VOLTS"
210  PRINT "4  -5.0 TO +5.0VOLTS"
220  PRINT "5  -1.0 TO +1.0VOLTS"
230  PRINT "6  -0.5 TO +0.5VOLTS"
240  PRINT "7  -0.1 TO +0.1VOLTS"
250  INPUT K
260  PRINT D$;"PR#1"
270  PRINT "RANGE #";K
280  PRINT D$;"PR#0"
290  POKE 32525 + I,K * 16 + I
300  PRINT "SELECT THE # OF REPLICATES FOR THIS     ARRAY (MAXIMUM 127"
310  PRINT "IF ARRAY NOT USED ENTER 0"
320  INPUT L
330  PRINT D$;"PR#1"
340  PRINT "# OF REPLICATES=";L
350  PRINT D$;"PR#0"
360  POKE 32531 + I,L
370  PRINT
380  PRINT
390  NEXT I
395  REM WAIT FOR THE ARRAYS TO BE CLEARED
400  HOME : INVERSE : VTAB 3: PRINT "WHEN THE SOURCE IS READY"
410  VTAB 6: PRINT "PRESS THE WHITE BUTTON ON THE GREY BOX"
420  VTAB 9: PRINT "WAIT UNTIL THE GREEN LIGHT COMES ON"
430  VTAB 12: PRINT "THEN PRESS ANY KEY TO COLLECT DATA"
440  NORMAL
450  CALL  - 756
455  PRINT "HERE WE GO"
460  REM RUN THE MACHINE CODE PROGRAM TO COLLECT DATA
470  PRINT  CHR$ (4);"BRUNMC2AA.OBJ0"
480  HOME
490  PRINT "CHOOSE:-"
495  PRINT
500  HTAB 7: PRINT "1. RETURN TO MAIN MENU"
```

```
510  PRINT
520  HTAB 7: PRINT "2. TRANSFER RAW DATA TO"
530  HTAB 10: PRINT "BACKGROUND STORAGE"
540  PRINT
550  HTAB 7: PRINT "3. CALCULATE MEANS FOR "
560  HTAB 10: PRINT "ANALYTE DATA"
570  PRINT
580  HTAB 7: PRINT "4. CALCULATE MEANS FOR "
590  HTAB 10: PRINT "BACKGROUND DATA"
595  PRINT
600  INPUT "ENTER 1,2,3 OR 4   ";E$
605 D$ =  CHR$ (4)
610  ON  VAL (E$) GOTO 620,640,650,660
620  PRINT D$;"RUNDRS"
640  PRINT D$;"BRUNMC2B.OBJ0"
645  GOTO 620
650  PRINT D$;"RUNSEL2A"
655  GOTO 620
660  PRINT D$;"RUNSEL2B"
670  GOTO 620
```

```
SOURCE FILE: MC2AA
----- NEXT OBJECT FILE NAME IS MC2AA.OBJ0
9200:                        ORG   $9200
9200:                  *PROGRAM TO READ ALL 6 ARRAYS AND RECORD DIGITISED VALUES
C400:                  PORT  EQU   $C400
C0B0:                  ADC   EQU   $C0B0
9200:D8                      CLD
9201:78                      SEI
9202:                  *COPY THE REPLICATION REQUIRED. 2ND SET TO BE DECREMENTED
9202:A2 05                   LDX   #$05
9204:BD 13 7F          BR1   LDA   $7F13,X
9207:9D 19 7F                STA   $7F19,X
920A:CA                      DEX
920B:10 F7                   BPL   BR1
920D:EA                      NOP
920E:EA                      NOP
920F:EA                      NOP
9210:                  *SIGNAL AVERAGING REQUIRES USE OF ADDITION.
9210:                  *STORAGE MEMORY MUST BE ZERO FILLED BEFORE DATA COLLECTION
9210:A9 01                   LDA   #$01
9212:8D 1B C4                STA   PORT+$1B   ;ENABLE PORT A LATCHES
9215:A2 00                   LDX   #$00
9217:A9 00                   LDA   #$00
9219:9D 00 80          BR2   STA   $8000,X
921C:9D 00 81                STA   $8100,X
921F:9D 00 82                STA   $8200,X
9222:9D 00 83                STA   $8300,X
9225:9D 00 84                STA   $8400,X
9228:9D 00 85                STA   $8500,X
922B:9D 00 86                STA   $8600,X
922E:9D 00 87                STA   $8700,X
9231:9D 00 88                STA   $8800,X
9234:CA                      DEX
9235:D0 E2                   BNE   BR2
9237:A9 00             BR4   LDA   #$00
9239:8D 13 C4                STA   PORT+$13   ;SET DDRA FOR INPUTS ON ORA
923C:                  *LOOK FOR THE RISING EDGE OF THE START PULSE
923C:A9 01                   LDA   #$01
923E:8D 1C C4                STA   PORT+$1C   ;SET PCR FOR RESPONSE ON CA1
9241:AD 11 C4                LDA   PORT+$11   ;BUT FIRST CLEAR THE IFR
9244:AD 1D C4          BR3   LDA   PORT+$1D   ;READ IFR
9247:29 02                   AND   #$02       ;CHECK FOR CA1 INTERRUPT FLAG
9249:F0 F9                   BEQ   BR3        ;IF NOT FOUND KEEP LOOKING
924B:                  *CLEAR IFR.READ ARRAY IDENTITY CODE FROM THE 74148 CHIP
924B:AD 11 C4                LDA   PORT+$11
924E:29 07                   AND   #$07       ;CLEAR UPPER 5 BITS
9250:8D 1F 7F                STA   $7F1F      ;STORE IT
9253:AA                      TAX              ;STORE ARRAY IDENTITY IN X REGISTER
9254:BD 19 7F                LDA   $7F19,X    ;LOAD THE REPLICATION COUNT
9257:F0 DE                   BEQ   BR4
9259:                  *IF DECREMENTED COUNTER IS ZERO REJECT THE START PULSE
9259:                  *AND LOOK FOR ANOTHER ONE
9259:30 DC                   BMI   BR4        ;A SAFETY TRAP IN CASE OF ACCIDENTS
925B:BD 0D 7F                LDA   $7F0D,X    ;SELECT THE GAIN CODE FOR THE ARRAY
925E:8D 24 7F                STA   $7F24      ;AND STORE IT
9261:                  *A DUMMY WRITE TO IS NOW MADE TO THE ADC TO GIVE THE CHANNEL
9261:                  *SWITCHES AND AMPLIFIERS TIME TO SETTLE.THE ADC IS SET TO
9261:                  *RESPOND TO A TRIGGER AND SET A FLAG WHEN DONE
9261:8D B3 C0                STA   ADC+3
9264:AD 1F 7F                LDA   $7F1F      ;LOAD WITH THE ARRAY IDENTITY CODE
```

```
9267:            59 *THE CODE IS NOW SHIFTED ONE BIT RIGHT.IF IT IS ODD THE
9267:            60 *CARRY FLAG IS SET.IF EVEN THE CARRY FLAG IS RESET
9267:4A          61         LSR  A
9268:            62 *SAVE THE UPPER BITS OF THE CODE IN THE X REGISTER
9268:AA          63         TAX
9269:            64 *THE LOW BYTE OF THE BASE ADDRESSES FOR DATA STORAGE ARE
9269:            65 *SELECTED ACCORDING TO THE STATE OF THE CARRY AND WRITTEN
9269:            66 *FORWARDS IN THE PROGRAM
9269:B0 16       67         BCS  BR5
926B:            68 *IF THE ARRAY IS EVEN THE LOW BYTE BASE ADDRESS IS $00
926B:A9 00       69         LDA  #$00
926D:8D D3 92    70         STA  ADD1+1
9270:8D D6 92    71         STA  ADD2+1
9273:8D DE 92    72         STA  ADD3+1
9276:8D E1 92    73         STA  ADD4+1
9279:8D E4 92    74         STA  ADD5+1
927C:8D E9 92    75         STA  ADD6+1
927F:F0 14       76         BEQ  BR6
9281:            77 *IF THE ARRAY IS ODD THE LOW BYTE BASE ADDRESS IS $80
9281:A9 80       78 BR5     LDA  #$80
9283:8D D3 92    79         STA  ADD1+1
9286:8D D6 92    80         STA  ADD2+1
9289:8D DE 92    81         STA  ADD3+1
928C:8D E1 92    82         STA  ADD4+1
928F:8D E4 92    83         STA  ADD5+1
9292:8D E9 92    84         STA  ADD6+1
9295:            85 *RELOAD WITH THE UPPER BITS OF THE ARRAY CODE AND ADD THEM TO
9295:            86 *THE STARTING ADDRESSES IN TURN TO GET THE HIGH BYTE BASE
9295:            87 *ADDRESSES FOR THE LOW,HIGH AND CARRY FILES FOR DATA
9295:            88 *STORAGE AND WRITE THEM FORWARDS IN THE PROGRAM
9295:8A          89 BR6     TXA
9296:18          90         CLC             ;CLEAR CARRY FLAG IF SET
9297:69 80       91         ADC  #$80
9299:8D D4 92    92         STA  ADD1+2
929C:8D D7 92    93         STA  ADD2+2
929F:8A          94         TXA
92A0:69 83       95         ADC  #$83
92A2:8D DF 92    96         STA  ADD3+2
92A5:8D E2 92    97         STA  ADD4+2
92A8:8A          98         TXA
92A9:69 86       99         ADC  #$86
92AB:8D E5 92   100         STA  ADD5+2
92AE:8D EA 92   101         STA  ADD6+2
92B1:           102 *LOOK FOR THE FALLING EDGE OF THE START PULSE
92B1:A9 00      103         LDA  #$00
92B3:8D 1C C4   104         STA  PORT+$1C  ;SET PCR FOR FALLING EDGES
92B6:AD 11 C4   105         LDA  PORT+$11  ;CLEAR THE IFR
92B9:AD 1D C4   106 BR7     LDA  PORT+$1D  ;READ IFR
92BC:29 02      107         AND  #$02      ;CHECK FOR CA1 INTERRUPT FLAG
92BE:F0 F9      108         BEQ  BR7       ;IF NOT FOUND KEEP LOOKING
92C0:A2 7F      109         LDX  #$7F      ;TO LOG 128 DIODES
92C2:AD 24 7F   110 BR9     LDA  $7F24     ;LOAD WITH THE GAIN CODE
92C5:8D B3 C0   111         STA  ADC+3     ;INITIATE CONVERSION AFTER TRIGGER
92C8:AD B1 C0   112 BR8     LDA  ADC+$1    ;LOOK FOR CONVERSION COMPLETED FLAG
92CB:29 80      113         AND  #$80      ;1 IN MSB IS DONE FLAG
92CD:F0 F9      114         BEQ  BR8       ;IF NOT DONE KEEP LOOKING
92CF:AD B0 C0   115         LDA  ADC       ;FETCH LOW BYTE OF CONVERSION
92D2:7D FF FF   116 ADD1    ADC  $FFFF,X   ;ADD IT TO DATA
92D5:9D FF FF   117 ADD2    STA  $FFFF,X   ;ALREADY COLLECTED
92D8:AD B1 C0   118         LDA  ADC+1     ;FETCH HIGH BYTE OF CONVERSION
```

```
92DB:29 0F       119            AND  #$0F      ;CLEAR OFF UPPER 4 BITS
92DD:7D FF FF    120 ADD3       ADC  $FFFF,X   ;ADD IT TO DATA
92E0:9D FF FF    121 ADD4       STA  $FFFF,X   ;ALREADY COLLECTED
92E3:BD FF FF    122 ADD5       LDA  $FFFF,X   ;LOAD THE CARRY BYTE
92E6:69 00       123            ADC  #$00      ;ADD THE CARRY FLAG IF SET
92E8:9D FF FF    124 ADD6       STA  $FFFF,X   ;UPDATE THE FILE
92EB:CA          125            DEX
92EC:10 D4       126            BPL  BR9       ;LOG ANOTHER DIODE IF NOT DONE
92EE:            127 *THE ARRAY HAS BEEN LOGGED. DECREMENT IT'S REPLICATE COUNT
92EE:AE 1F 7F    128            LDX  $7F1F     ;LOAD WITH THE ARRAY CODE
92F1:DE 19 7F    129            DEC  $7F19,X   ;DECREMENT THE CORRECT REPLICATE COUNT
92F4:            130 *NOW TEST FOR COMPLETION OF ALL REQUESTED ARRAYS AND RUNS
92F4:18          131            CLC
92F5:AD 19 7F    132            LDA  $7F19
92F8:6D 1A 7F    133            ADC  $7F1A
92FB:6D 1B 7F    134            ADC  $7F1B
92FE:6D 1C 7F    135            ADC  $7F1C
9301:6D 1D 7F    136            ADC  $7F1D
9304:6D 1E 7F    137            ADC  $7F1E
9307:B0 02       138            BCS  BRB
9309:F0 03       139            BEQ  BRA
930B:4C 37 92    140 BRB        JMP  BR4       ;IF NOT DONE GO AGAIN
930E:60          141 BRA        RTS            ;BACK TO BASIC WHEN FINISHED


SOURCE FILE: MC2B
----- NEXT OBJECT FILE NAME IS MC2B.OBJ0
9200:              1            ORG  $9200
9200:              2 *TRANSFER RAW DATA FROM INPUT BUFFER TO BACKGROUND RAW DATA
9200:              3 *MEMORY SPACE.THIS LEAVES THE INPUT BUFFER FREE
9200:18            4            CLC
9201:A2 00         5            LDX  #$00
9203:BD 00 80      6 BR1        LDA  $8000,X
9206:9D 00 89      7            STA  $8900,X
9209:BD 00 81      8            LDA  $8100,X
920C:9D 00 8A      9            STA  $8A00,X
920F:BD 00 82     10            LDA  $8200,X
9212:9D 00 8B     11            STA  $8B00,X
9215:BD 00 83     12            LDA  $8300,X
9218:9D 00 8C     13            STA  $8C00,X
921B:BD 00 84     14            LDA  $8400,X
921E:9D 00 8D     15            STA  $8D00,X
9221:BD 00 85     16            LDA  $8500,X
9224:9D 00 8E     17            STA  $8E00,X
9227:BD 00 86     18            LDA  $8600,X
922A:9D 00 8F     19            STA  $8F00,X
922D:BD 00 87     20            LDA  $8700,X
9230:9D 00 90     21            STA  $9000,X
9233:BD 00 88     22            LDA  $8800,X
9236:9D 00 91     23            STA  $9100,X
9239:CA           24            DEX
923A:D0 C7        25            BNE  BR1
923C:             26 *NOW TRANSFER THE GAIN AND REPLICATION DATA
923C:A2 17        27            LDX  #$17
923E:BD 01 7F     28 BR2        LDA  $7F01,X
9241:9D 26 7F     29            STA  $7F26,X
9244:CA           30            DEX
9245:10 F7        31            BPL  BR2
9247:60           32            RTS
```

```
1  REM PROGRAM **SEL2A**
5  HIMEM: 29439
10  REM THIS OPTION CALCULATES MEANS FROM DATA IN THE INPUT BUFFER
12  REM AND STORES THEM IN THE ANALYTE MEANS FILE
20 D$ =  CHR$ (4)
30 AA = 32768:B = 128:C = 768:D = 1536:E = 32531:F = 30976:S = 256
120  FOR I = 0 TO 5
125 W = F + I * B:X = W + C
130 A = AA + I * B:K = A + C:L = A + D:M =  PEEK (E + I)
135  IF M = 0 THEN 200
140  FOR N = 0 TO 127
150 O =  PEEK (A + N):P =  PEEK (K + N):Q =  PEEK (L + N)
160 R = ((Q * S + P) * S + O) / M:T =  INT (R / S)
170 U =  INT (R - S * T)
180  POKE W + N,U: POKE X + N,T
190  NEXT N
200  NEXT I
210  PRINT D$;"BRUNMC5.OBJ0"
220  PRINT D$;"RUNSEL2"
```

```
SOURCE FILE: MC5
----- NEXT OBJECT FILE NAME IS MC5.OBJ0
9200:               1          ORG  $9200
9200:               2 *TRANSFER REPLICATION AND GAIN DATA
9200:               3 *FOR ANALYTE MEANS FILE
9200:               4 *FROM THE INPUT BUFFER
9200:A2 17          5          LDX  #$17
9202:BD 01 7F       6 BR1      LDA  $7F01,X
9205:9D 3E 7F       7          STA  $7F3E,X
9208:CA             8          DEX
9209:10 F7          9          BPL  BR1
920B:60            10          RTS
```

```
1  REM PROGRAM**SEL2B**
5  HIMEM: 29439
10  REM THIS OPTION CALCULATES MEANS FROM DATA IN THE INPUT BUFFER
12  REM  AND STORES THEM IN THE BACKGROUND MEANS FILE
20 D$ =  CHR$ (4)
30 AA = 32768:B = 128:C = 768:D = 1536:E = 32531:F = 29440:S = 256
120  FOR I = 0 TO 5
125 W = F + I * B:X = W + C
130 A = AA + I * B:K = A + C:L = A + D:M =  PEEK (E + I)
135  IF M = 0 THEN 200
140  FOR N = 0 TO 127
150 O =  PEEK (A + N):P =  PEEK (K + N):Q =  PEEK (L + N)
160 R = ((Q * S + P) * S + O) / M:T =  INT (R / S)
170 U =  INT (R - S * T)
180  POKE W + N,U: POKE X + N,T
190  NEXT N
200  NEXT I
210  PRINT D$;"BRUNMC6.OBJ0"
220  PRINT D$;"RUNSEL2"
```

```
SOURCE FILE: MC6
----- NEXT OBJECT FILE NAME IS MC6.OBJ0
9200:             1          ORG  $9200
9200:             2 *TRANSFER REPLICATION AND GAIN DATA
9200:             3 *FOR BACKGROUND MEANS FILE
9200:             4 *FROM THE INPUT BUFFER
9200:A2 17        5          LDX  #$17
9202:BD 01 7F     6 BR1      LDA  $7F01,X
9205:9D 56 7F     7          STA  $7F56,X
9208:CA           8          DEX
9209:10 F7        9          BPL  BR1
920B:60          10          RTS
```

SEL3 is similar to SEL1 except that it runs one array for a short integration time (down to 0.018 s) while the other 5 arrays stay at 205 s integration.

MC10.OBJ0 loads zero as default values in the integration time scratch pad addresses. The BASIC program then corrects the scratch pad addresses for the array of interest.

MC10B.OBJ0 is similar to MC1BA.OBJ0 except that it does not check for obedience of the readout clash prevention rules.

```
10  REM PROGRAM **SEL3**
20  HIMEM: 29439
30  HOME
40  PRINT "THIS OPTION RUNS A SINGLE ARRAY"
50  PRINT
60  PRINT "WITH A SHORT INTEGRATION TIME"
70  PRINT
80  PRINT "THE OTHER 5 ARRAYS ARE LEFT WITH"
90  PRINT
100  PRINT "A 205 SECOND INTEGRATION TIME"
110  PRINT
120  PRINT "THE SELECTED ARRAY CAN BE READ"
130  PRINT
140  PRINT "OUT AFTER A MINIMUM OF 0.018"
150  PRINT
160  PRINT "SECONDS"
170  PRINT
180  FOR X = 0 TO 5000: NEXT X
190  PRINT "THIS SERVES 2 PURPOSES:-"
200  PRINT
210  HTAB 4: PRINT "1. GIVES A HIGH REFRESHMENT"
220  PRINT
230  HTAB 7: PRINT "RATE FOR AN OSCILLOSCOPE"
240  PRINT
250  HTAB 7: PRINT "DURING ARRAY SET UP"
260  PRINT
270  HTAB 4: PRINT "2. ALLOWS DATA COLLECTION"
280  PRINT
290  HTAB 7: PRINT "FOR A VERY STRONG SIGNAL"
300  REM FORCE DEFAULT INTEGRATION TIMES OF 205 SECONDS INTO SCRATCH PAD MEMORY
310  PRINT  CHR$ (4);"BRUNMC10.OBJ0"
320  PRINT
330  PRINT
340  PRINT
350  HTAB 4: PRINT "ENTER ARRAY # FOR SHORT"
360  PRINT
370  HTAB 4: PRINT "INTEGRATION TIME  ": INPUT I
380  PRINT
390  PRINT
400  HTAB 4: PRINT "ENTER IT'S INTEGRATION TIME"
410  PRINT
420  HTAB 4: PRINT "IN SECONDS  ": INPUT B
430 E = 0.5:F = 256:D = 3.1281E - 3:H = 32
440 C =  INT (B / D + E)
450 T = C / F:G =  INT (T)
460 J =  INT (F * (T - G) + E)
470  IF G > 255 THEN  PRINT "TOO LONG": GOTO 400
480  IF G > 0 THEN 510
490  IF J < 6 THEN  PRINT "TOO SHORT": GOTO 400
500  REM FORCE INTEGRATION TIME INTO SCRATCH PAD MEMORY
510  POKE 32513 + 2 * I,J: POKE 32514 + 2 * I,G
520 L = (J + F * G) * D
530 L =  INT (L * 10 ^ 4 + .5) /  INT (10 ^ 4 + .5)
540  PRINT  CHR$ (4);"PR#1"
550  PRINT "ACTUAL INTEGRATION TIME ARRAY# ";I;"=";L;"SECONDS"
560  PRINT  CHR$ (4);"PR#0"
570  PRINT  CHR$ (4);"BRUNMC10B.OBJ0"
580  PRINT  CHR$ (4);"RUNDRS"
```

```
SOURCE FILE: MC10B
0000:              ****MC10B****
0000:              *SET UP A SHORT INTEGRATION TIME FOR A SINGLE ARRAY
0000:              *PART OF PROGRAM FOR SETTING INTEGRATION TIMES FOR 6 ARRAYS
0000:              *THE BASIC PROGRAM HAS PREVIOUSLY POKED THE INTEGRATION TIMES
 INTO SCRATCH PAD MEMORY
----- NEXT OBJECT FILE NAME IS MC10B.OBJ0
9237:                       ORG  $9237
9237:              *CLOSE THE GATE ON 8253 #1 COUNTER 0 DURING LOADING
9237:AD 58 C0               LDA  $C058
C0D0:              CLK      EQU  $C0D0
923A:              *FOR 8253 # 1
923A:A9 34                  LDA  #$34       ;LOAD MODE WORD COUNTER 0 MODE 2
923C:8D D3 C0               STA  CLK+3      ;LOAD INTO 8253 #1
923F:A9 50                  LDA  #$50       ;LOAD MODE WORD COUNTER 1 MODE 0
9241:8D D3 C0               STA  CLK+3      ;LOAD INTO 8253 #1
9244:A9 90                  LDA  #$90       ;LOAD MODE WORD COUNTER " MODE 2
9246:8D D3 C0               STA  CLK+3      ;LOAD INTO 8253 #1
9249:              *COUNTER #0 IN MODE 2 DIVIDES CLOCK RATE BY 3200
9249:A9 80                  LDA  #$80       ;LOAD COUNTER 0 LOW BYTE
924B:8D D0 C0               STA  CLK        ;WRITE LOW BYTE
924E:A9 0C                  LDA  #$0C       ;LOAD COUNTER 0 HIGH BYTE
9250:8D D0 C0               STA  CLK        ;WRITE HIGH BYTE
9253:              *COUNTERS #1 AND 2 OF 8253 #1 AND ALL 3 COUNTERS OF 8253 #2
9253:              *ARE IN MODE 0.THEY GATE COUNTERS #1 AND 2 OF 8253 #3 AND
9253:              *ALL 3 COUNTERS OF 8253 #4 THEREBY DELAYING THE START OF
9253:              *THEIR COUNTS
9253:A9 04                  LDA  #$04       ;LOAD COUNTER 1 LOW BYTE (ONLY)
9255:8D D1 C0               STA  CLK+1      ;WRITE LOW BYTE (ONLY)
9258:A9 09                  LDA  #$09       ;LOAD COUNTER 2 LOW BYTE (ONLY)
925A:8D D2 C0               STA  CLK+2      ;WRITE LOW BYTE (ONLY)
925D:              *FOR 8253 # 2
925D:A9 10                  LDA  #$10       ;LOAD MODE WORD COUNTER 0 MODE 0
925F:8D D7 C0               STA  CLK+7      ;LOAD INTO 8253 #2
9262:A9 50                  LDA  #$50       ;LOAD MODE WORD COUNTER 1 MODE 0
9264:8D D7 C0               STA  CLK+7      ;LOAD INTO 8253 #2
9267:A9 90                  LDA  #$90       ;LOAD MODE WORD COUNTER 2 MODE 0
9269:8D D7 C0               STA  CLK+7      ;LOAD INTO 8253 #2
926C:A9 0F                  LDA  #$0F       ;LOAD COUNTER 0 LOW BYTE (ONLY)
926E:8D D4 C0               STA  CLK+4      ;WRITE LOW BYTE (ONLY)
9271:A9 14                  LDA  #$14       ;LOAD COUNTER 1 LOW BYTE (ONLY)
9273:8D D5 C0               STA  CLK+5      ;WRITE LOW BYTE (ONLY)
9276:A9 19                  LDA  #$19       ;LOAD COUNTER 2 LOW BYTE (ONLY)
9278:8D D6 C0               STA  CLK+6      ;WRITE LOW BYTE (ONLY)
927B:              *8253'S #3 AND 4 CONTROL THE ACTUAL INTEGRATION TIMES.
927B:              *AFTER MODE WORDS ARE LOADED (ALL COUNTERS IN MODE 2)
927B:              *THE COUNTERS ARE LOADED WITH THEIR COUNTS FROM SCRATCH
927B:              *PAD MEMORY,WHERE THEY WERE PLACED BY THE BASIC PROGRAM
927B:A9 34                  LDA  #$34       ;LOAD MODE WORD COUNTER 0 MODE 2
927D:8D DB C0               STA  CLK+$B     ;LOAD INTO 8253 #3
9280:A9 74                  LDA  #$74       ;LOAD MODE WORD COUNTER 1 MODE 2
9282:8D DB C0               STA  CLK+$B     ;LOAD INTO 8253 #3
9285:A9 B4                  LDA  #$B4       ;LOAD MODE WORD COUNTER 2 MODE 2
9287:8D DB C0               STA  CLK+$B     ;LOAD INTO 8253 #3
928A:AD 01 7F               LDA  $7F01      ;FETCH LOW BYTE 1ST INTEGRATION TIME
928D:8D D8 C0               STA  CLK+8      ;WRITE LOW BYTE
9290:AD 02 7F               LDA  $7F02      ;FETCH HIGH BYTE 1ST INTEGRATION TIME
9293:8D D8 C0               STA  CLK+8      ;WRITE HIGH BYTE
9296:AD 03 7F               LDA  $7F03      ;FETCH LOW BYTE 2ND INTEGRATION TIME
9299:8D D9 C0               STA  CLK+9      ;WRITE LOW BYTE
929C:AD 04 7F               LDA  $7F04      ;FETCH HIGH BYTE 2ND INTEGRATION TIME
```

```
929F:8D D9 C0    59        STA  CLK+9       ;WRITE HIGH BYTE
92A2:AD 05 7F    60        LDA  $7F05       ;FETCH LOW BYTE 3RD INTEGRATION TIME
92A5:8D DA C0    61        STA  CLK+$A      ;WRITE LOW BYTE
92A8:AD 06 7F    62        LDA  $7F06       ;FETCH HIGH BYTE 3RD INTEGRATION TIME
92AB:8D DA C0    63        STA  CLK+$A      ;WRITE HIGH BYTE
92AE:A9 34       64        LDA  #$34        ;LOAD MODE WORD COUNTER 0 MODE 2
92B0:8D DF C0    65        STA  CLK+$F      ;LOAD INTO 8253 #4
92B3:A9 74       66        LDA  #$74        ;LOAD MODE WORD COUNTER 0 MODE2
92B5:8D DF C0    67        STA  CLK+$F      ;LOAD INTO 8253 #4
92B8:A9 B4       68        LDA  #$B4        ;LOAD MODE WORD COUNTER 0 MODE 2
92BA:8D DF C0    69        STA  CLK+$F      ;LOAD INTO 8253 #4
92BD:AD 07 7F    70        LDA  $7F07       ;FETCH LOW BYTE 4TH INTEGRATION TIME
92C0:8D DC C0    71        STA  CLK+$C      ;WRITE LOW BYTE
92C3:AD 08 7F    72        LDA  $7F08       ;FETCH HIGH BYTE 4TH INTEGRATION TIME
92C6:8D DC C0    73        STA  CLK+$C      ;WRITE HIGH BYTE
92C9:AD 09 7F    74        LDA  $7F09       ;FETCH LOW BYTE 5TH INTEGRATION TIME
92CC:8D DD C0    75        STA  CLK+$D      ;WRITE LOW BYTE
92CF:AD 0A 7F    76        LDA  $7F0A       ;FETCH HIGH BYTE 5TH INTEGRATION TIME
92D2:8D DD C0    77        STA  CLK+$D      ;WRITE HIGH BYTE
92D5:AD 0B 7F    78        LDA  $7F0B       ;FETCH LOW BYTE 6TH INTEGRATION TIME
92D8:8D DE C0    79        STA  CLK+$E      ;WRITE LOW BYTE
92DB:AD 0C 7F    80        LDA  $7F0C       ;FETCH HIGH BYTE 6TH INTEGRATION TIME
92DE:8D DE C0    81        STA  CLK+$E      ;WRITE HIGH BYTE
92E1:EA          82        NOP
92E2:EA          83        NOP
92E3:EA          84        NOP
92E4:            85 *ALL COUNTERS LOADED SO OPEN THE GATE ON 8253 #1 COUNTER 0
92E4:AD 59 C0    86        LDA  $C059
92E7:60          87        RTS              ;GO AND DO SOMETHING ELSE
```

```
SOURCE FILE: MC10
----- NEXT OBJECT FILE NAME IS MC10.OBJ0
9205:             1          ORG  $9205
9205:             2 *PROGRAM TO PUT DEFAULT VALUES IN SCRATCH PAD MEMORY
9205:             3 *LOAD BOTH BYTES WITH MAXIMUM (=0)
9205:A9 00        4          LDA  #$00       ;LOAD LOW BYTE
9207:8D 01 7F     5          STA  $7F01
920A:8D 03 7F     6          STA  $7F03
920D:8D 05 7F     7          STA  $7F05
9210:8D 07 7F     8          STA  $7F07
9213:8D 09 7F     9          STA  $7F09
9216:8D 0B 7F    10          STA  $7F0B
9219:A9 00       11          LDA  #$00       ;LOAD HIGH BYTE
921B:8D 02 7F    12          STA  $7F02
921E:8D 04 7F    13          STA  $7F04
9221:8D 06 7F    14          STA  $7F06
9224:8D 08 7F    15          STA  $7F08
9227:8D 0A 7F    16          STA  $7F0A
922A:8D 0C 7F    17          STA  $7F0C
922D:60          18          RTS             ;FINISHED
```

SEL4 is used to subtract 2 sets of data values. If necessary it calculates the mean values first. It can take its data from the RAM data files or can load it from disk storage. Before doing the subtraction, it checks for matching of the gain code of the A/DC and the integration time used for each array and aborts if it finds a mismatch.

TEST.OBJ0 is just a dummy program that acts as a switch, changing the drive response from drive #2, the data disk, back to drive #1, for the system disk.

MC6A transfers replication and gain data to the Background Means File from the Background Raw Data File.

MC7.OBJ0 is the binary subtraction program.

```
10  REM PROGRAM **SEL4**
20  HIMEM: 29439
30  GOTO 280
40  REM BACKGROUND SUBTRACTION PROGRAM
50  REM SUBROUTINE TO CALCULATE MEANS FROM DATA IN THE INPUT BUFFER
60  REM OR BACKGROUND RAW DATA FILE AND STORE THEM IN THE ANALYTE OR BACKGROUND
70  REM MEANS FILE
80  PRINT
90 B = 128:C = 768:D = 1536:S = 256
100 AA = A
110  REM  ONE ARRAY AT A TIME
120  FOR I = 0 TO 5
130 W = F + I * B:X = W + C
140 A = AA + I * B:K = A + C:L = A + D:M =  PEEK (E + I)
150  REM CHECK THE REPLICATE COUNT.IF ZERO IGNORE THIS ARRAY
160  IF M = 0 THEN 260
170  FOR N = 0 TO 127
180 O =  PEEK (A + N):P =  PEEK (K + N):Q =  PEEK (L + N)
190  REM READ THE DATA FILE IN DECIMAL
200 R = ((Q * S + P) * S + O) / M:T =  INT (R / S)
210  REM DIVIDE BY THE REPLICATE COUNT AND PUT IT BACK IN A
220  REM TWO BYTE BINARY FORM
230 U =  INT (R - S * T)
240  POKE W + N,U: POKE X + N,T
250  NEXT N
260  NEXT I
270  RETURN
280  HOME
290  INVERSE : HTAB 4: PRINT "BACKGROUND SUBTRACTION OPTION": NORMAL
300  PRINT "THIS OPTION SUBTRACTS ONE SET OF DATA   POINT MEANS FROM ANOTHER SET
310  PRINT
320  HTAB 15: INVERSE : PRINT "WARNING": NORMAL
330  PRINT
340  PRINT "THIS PROGRAM OVERWRITES THE INPUT BUFFER"
350  PRINT "IF YOU WISH TO KEEP IT'S CONTENTS AS RAW"
360  PRINT "DATA, ABORT THIS PROGRAM NOW AND SAVE "
370  PRINT
380  PRINT "THE BUFFER ON DISKETTE FIRST"
390  PRINT "****************************************"
400  FOR X = 1 TO 4000: NEXT X
410  PRINT "WHERE IS THE BACKGROUND DATA ?"
420  PRINT
430  PRINT "1. IN THE INPUT DATA BUFFER ?"
440  PRINT
450  PRINT "2. IN THE BACKGROUND RAW DATA FILE ?"
460  PRINT
470  PRINT "3. IN THE BACKGROUND MEANS FILE ?"
480  PRINT
490  PRINT "4. ON DISK AS RAW DATA ?"
500  PRINT
510  PRINT "5. ON DISK AS MEANS ?"
520  PRINT
530  INPUT "ENTER 1,2,3,4 OR 5  ";A$
540  HOME
550  PRINT "WHERE IS THE ANALYTE DATA ?"
560  PRINT
570  PRINT "1. IN THE INPUT BUFFER ?"
580  PRINT
590  PRINT "2. IN THE ANALYTE MEANS FILE ?"
600  PRINT
```

```
610  PRINT "3. ON DISK AS RAW DATA ?"
620  PRINT
630  PRINT "4. ON DISK AS MEANS ?  "
640  PRINT
650  INPUT "ENTER 1,2,3 OR 4  ";B$
660  ON  VAL (A$) GOTO 680,720,750,760,840
670  PRINT
680 A = 32768:E = 32531:F = 29440
690  GOSUB 80
700  PRINT  CHR$ (4);"BRUNMC6.OBJ0"
710  GOTO 890
720 A = 35072:E = 32568:F = 29440
730  GOSUB 80
740  PRINT  CHR$ (4);"BRUNMC6A.OBJ0"
750  GOTO 890
760  INPUT "ENTER BACKGROUND FILE NAME  ";F$
770 G$ = F$ + "Z"
780  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$8900"
790  PRINT  CHR$ (4);"BLOAD";G$;",A$7F26"
800 A = 35072:E = 32568:F = 29440
810  GOSUB 80
820  PRINT  CHR$ (4);"BRUNMC6A.OBJ0,D1"
830  GOTO 890
840  INPUT "ENTER BACKGROUND FILE NAME  ";F$
850 G$ = F$ + "Z"
860  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$7300"
870  PRINT  CHR$ (4);"BLOAD";G$;",A$7F56"
880  PRINT  CHR$ (4);"BLOADTEST,D1"
890  ON  VAL (B$) GOTO 900,930,940,1020
900 A = 32768:E = 32531:F = 30976
910  GOSUB 80
920  PRINT  CHR$ (4);"BRUNMC5.OBJ0"
930  GOTO 1070
940  INPUT "ENTER ANALYTE FILE NAME  ";F$
950 G$ = F$ + "Z"
960  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$8000"
970  PRINT  CHR$ (4);"BLOAD";G$;",A$7F01"
980 A = 32768:E = 32531:F = 30976
990  GOSUB 80
1000  PRINT  CHR$ (4);"BRUNMC5.OBJ0,D1"
1010  GOTO 1070
1020  INPUT "ENTER ANALYTE FILE NAME  ";F$
1030 G$ = F$ + "Z"
1040  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$7900"
1050  PRINT  CHR$ (4);"BLOAD";G$;",A$7F3E"
1060  PRINT  CHR$ (4);"BLOADTEST,D1"
1070  REM NOW THAT THE FILES ARE IN THEIR PROPER LOCATIONS THEY MUST BE TESTED
1080  REM TO SEE IF SUBTRACTION WOULD BE LEGITIMATE
1090 H = 32586:J = 32610
1100  FOR I = 0 TO 5:G =  PEEK (H + I) -  PEEK (J + I)
1110  IF G = 0 GOTO 1140
1120  FLASH : PRINT "ARRAY ";I;"GAINS DO NOT MATCH": NORMAL
1130  PRINT  CHR$ (4);"RUNDRS"
1140 H = 32574:J = 32598
1150  FOR I = 0 TO 5:G =  PEEK (H + 2 * I) -  PEEK (J + 2 * I)
1160 V =  PEEK (H + 2 * I + 1) -  PEEK (J + 2 * I + 1)
1170  IF G <  > 0 GOTO 1200
1180  IF V <  > 0 GOTO 1200
1190  GOTO 1220
1200  FLASH : PRINT "INTEGRATION TIMES DO NOT MATCH": NORMAL
```

```
1210  PRINT  CHR$ (4);"RUNDRS"
1220  NEXT I
1230  REM  AS ALL IS WELL DO THE SUBTRACTION
1240  PRINT  CHR$ (4);"BRUNMC7.OBJ0"
1250 E = 32531: FOR I = 0 TO 5: POKE E + I,1: NEXT I
1260  REM DIFFERENCES ARE STORED IN INPUT BUFFER.REPLICATION VALUE
1270  REM REDUCED TO 1 TO AVOID PROBLEMS
1280  HOME
1290  PRINT "BACKGROUND SUBTRACTED VALUES ARE"
1300  PRINT
1310  PRINT "IN THE INPUT BUFFER IN BINARY"
1320  PRINT
1330  INVERSE : PRINT "THERE WILL BE OVERSUBTRACTION DUE TO"
1340  PRINT
1350  PRINT "NOISE.THIS MUST BE CORRECTED FOR IN"
1360  PRINT
1370  PRINT "THE READOUT OPTIONS"
1380  PRINT
1390  NORMAL
1400  PRINT "CHOOSE:-"
1410  PRINT
1420  PRINT "1. STORE ON DISKETTE"
1430  PRINT
1440  PRINT "2. OUTPUT USING AN OPTION ON THE"
1450  HTAB 4: PRINT "MAIN MENU"
1460  PRINT
1470  INPUT "CHOOSE 1 OR 2  ";K$
1480  ON  VAL (K$) GOTO 1490,1550
1490  HOME
1500  INPUT "ENTER FILE NAME";F$
1510 G$ = F$ + "Z"
1520  PRINT  CHR$ (4);"BSAVED";F$;",D2,A$8000,L$600"
1530  PRINT  CHR$ (4);"BSAVED";G$;",A$7F01,L$18"
1540  GOTO 1360
1550  PRINT  CHR$ (4);"RUNDRS,D1"
```

```
SOURCE FILE: TEST
----- NEXT OBJECT FILE NAME IS TEST.OBJ0
95F8:                         ORG  $95F8
95F8:               *TEST A PROGRAM THAT ACOMPLISHES NOTHING BUT IS USED IN A
95F8:               *DOS COMMAND TO SWITCH DISK DRIVES
95F8:AD FF 95                 LDA  $95FF
95FB:8D FF 95                 STA  $95FF
95FE:60                       RTS
```

```
SOURCE FILE: MC6A
----- NEXT OBJECT FILE NAME IS MC6A.OBJ0
9200:                         ORG  $9200
9200:               *TRANSFER REPLICATION AND GAIN DATA
9200:               *FOR THE BACKGROUND MEANS FILE
9200:               *FROM THE BACKGROUND RAW DATA FILE
9200:A2 17                    LDX  #$17
9202:BD 26 7F        BR1      LDA  $7F26,X
9205:9D 56 7F                 STA  $7F56,X
9208:CA                       DEX
9209:10 F7                    BPL  BR1
920B:60                       RTS
```

```
SOURCE FILE: MC7
----- NEXT OBJECT FILE NAME IS MC7.OBJ0
9200:               1        ORG  $9200
9200:               2 *PROGRAM SUBTRACTS THE TWO BYTE VALUES IN THE BACKGROUND
9200:               3 *MEANS FILE FROM THE TWO BYTE VALUES IN THE ANALYTE MEANS
9200:               4 *FILE AND STORES THE RESULT IN THE INPUT BUFFER
9200:D8             5        CLD
9201:A2 00          6        LDX  #$00
9203:38             7 BR1    SEC
9204:BD 00 79       8        LDA  $7900,X
9207:FD 00 73       9        SBC  $7300,X
920A:9D 00 80      10        STA  $8000,X
920D:BD 00 7C      11        LDA  $7C00,X
9210:FD 00 76      12        SBC  $7600,X
9213:9D 00 83      13        STA  $8300,X
9216:38            14        SEC
9217:BD 00 7A      15        LDA  $7A00,X
921A:FD 00 74      16        SBC  $7400,X
921D:9D 00 81      17        STA  $8100,X
9220:BD 00 7D      18        LDA  $7D00,X
9223:FD 00 77      19        SBC  $7700,X
9226:9D 00 84      20        STA  $8400,X
9229:38            21        SEC
922A:BD 00 7B      22        LDA  $7B00,X
922D:FD 00 75      23        SBC  $7500,X
9230:9D 00 82      24        STA  $8200,X
9233:BD 00 7E      25        LDA  $7E00,X
9236:FD 00 78      26        SBC  $7800,X
9239:9D 00 85      27        STA  $8500,X
923C:CA            28        DEX
923D:D0 C4         29        BNE  BR1
923F:              30 *NOW COPY THE INTEGRATION TIME,GAIN AND REPLICATION PARAMETER
S
923F:              31 *TO THE CORRESPONDING ADDRESSES FOR THE INPUT BUFFER
923F:A2 17         32        LDX  #$17
9241:BD 3E 7F      33 BR2    LDA  $7F3E,X
9244:9D 01 7F      34        STA  $7F01,X
9247:CA            35        DEX
9248:10 F7         36        BPL  BR2
924A:60            37        RTS            ;BACK TO BASIC
```

SEL5 is the graphics program. It allows display of the contents of a data file, array by array, on the video monitor. It can accept data from a disk. If the data file is the result of a subtraction and involves a bipolar A/DC setting (for example ± .5 V) it adds an offset value to recentre the spectrum. The program contains unlisted control characters which can be seen by first running a special decode program given in the Apple literature [60] and then loading the program from disk and listing it. The characters printed in lines 1040 to 1080 and 1130 are actually index marks on the graph abscissa and ordinate (the HTAB function does not quite match the required spacing of the abscissa index marks in high resolution graphics).

The program allows the video display to include a title and this version also displays the integration time, calculated from scratch pad memory values.

The display can be put out to a printer. The format for the display is shown in Figure 60.

One problem with the program is that once high resolution graphics are in use, the only way to leave them and return to standard text display is by pressing RESET. This unfortunately cancels the operation of the integration timers so they have to be reloaded through SEL1.

```
10  REM  PROGRAM **SEL5** CONTAINS UNLISTED CONTROL CHARACTERS
20  HIMEM: 29439
30  REM PROGRAM TO DISPLAY THE SIGNALS GRAPHICALLY ON THIS SCREEN
40  HOME
50 V = 0
60  REM  SET FLAG FOR HIRES CHAR SET TO BE LOADED
70 OS = 0
80  PRINT "THIS OPTION DISPLAYS THE OUTPUTS FOR ALL 128 DIODES OF A SELECTED ARR
AY ON THIS SCREEN"
90  PRINT : PRINT : PRINT "DATA CAN BE:-"
100  PRINT "1. SINGLE RUN IN THE INPUT BUFFER"
110  PRINT : PRINT "2. SINGLE RUN IN THE INPUT BUFFER"
120  HTAB 4: PRINT "FILE"
130  PRINT : PRINT "3. SUBTRACTED MEAN VALUES STORED"
140  HTAB 4: PRINT "IN THE INPUT BUFFER"
150  PRINT : PRINT "4. ANALYTE SIGNAL MEANS": PRINT
160  PRINT "5. BACKGROUND MEAN VALUES"
170  PRINT : PRINT "6. FROM A DISKETTE IN DRIVE #2": PRINT
180  PRINT
190  INPUT "ENTER 1,2,3,4,5 OR 6  ";E$
200  ON  VAL (E$) GOTO 220,230,240,250,260,270
210  REM F=BASE ADDRESS FOR THE GAIN CODES AND G= BASE ADDRESS FOR THE DATA
220 F = 32525:G = 32768: GOTO 340
230 F = 32562:G = 35072: GOTO 340
240 F = 32525:G = 32768:OS = 2048: GOTO 340
250 F = 32586:G = 30976: GOTO 340
260 F = 32610:G = 29440: GOTO 340
270  INPUT "ENTER FILE NAME  ";F$
280  REM LOAD FROM DISKETTE TO INPUT BUFFER
290 G$ = F$ + "Z"
300  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$8000"
310  PRINT  CHR$ (4);"BLOAD";G$;",A$7F01"
320  PRINT  CHR$ (4);"BLOADTEST,D1"
330 F = 32525:G = 32768
340 N = 256
350  IF V = 0 THEN  GOSUB 650
360  GOSUB 790
370  REM LOAD CHARACTER SETS FOR HIGH RESOLUTION GRAPHICS
380  GOSUB 920
390  REM  IDENTIFY INDIVIDUAL ARRAY AND DECODE GAIN CODE
400 B$ = "0"
410  REM RUN THE DISPLAY
420  PRINT B$
430  CALL  - 756
440  PRINT : PRINT "CHOOSE ONE OF THE FOLLOWING": PRINT
450  HTAB 4: PRINT "1. MAKE A PRINTED COPY OF THE GRAPH"
460  PRINT : HTAB 4: PRINT "2. LOOK AT ANOTHER ARRAY IN THE SAME    RUN": PRINT
470  HTAB 4: PRINT "3. LOOK AT ANOTHER FILE"
480  PRINT : HTAB 4: PRINT "4. CHOOSE AN ALTERNATIVE OUTPUT FROM    THE MAIN MEN
U": PRINT
490  PRINT
500  INPUT "ENTER 1,2,3 OR 4 ";Z
510  PRINT
520  PRINT
530  PRINT
540  PRINT
550  IF Z > 1 THEN 1390
560 Z$ = "G"
570  REM Z$=G FOR GRAPPLER AND RCSA FOR SAK API
580  GOSUB 920
590  PRINT  CHR$ (4);"PR#1"
```

```
600  PRINT  CHR$ (9);Z$
610  PRINT  CHR$ (4)"PR#0"
620  CALL ADRS
630  GOTO 400
640  REM  PROGRAM TO LOAD HRCG
650 ADRS = 0
660  PRINT  CHR$ (4);"BLOAD RBOOT"
670  CALL 520: REM  EXECUTE RBOOT
680 ADRS =  USR (0),"HRCG"
690  REM  BRING IN HRCG, ADRS=STARTING ADDRESS
700  IF ADRS <  = 0 THEN ADRS = ADRS + 65536: REM  MAKE ADRS POSITIVE
710 CS = ADRS - 768: HIMEM: CS
720 CH =  INT (CS / 256):CL = CS - 256 * CH
730  POKE ADRS + 7,CL: POKE ADRS + 8,CH
740  PRINT  CHR$ (4);"BLOADA.SET,A";CS
750  REM SET.A IS A MODIFIED ASCII SET WITH INDEX MARKS AS SPECIAL CHARACTERS
760 V = 1
770  REM  SET FLAG TO SHOW HIRES CHAR SET IS LOADED
780  RETURN
790  INPUT "ENTER ARRAY # ( 0 TO 5 )   ";I
800  REM DECODE GAIN CODE FOR ARRAY TO GET CONSTANTS FOR THE DISPLAY ORDINATE
810 W = 1:D = 3.1289E - 3:A1 = 12:H =  PEEK (F - A1 + I + I) + N *  PEEK (F - A1
 + I + I + W):H2 = H * D:H2 =  INT (H2 * 10 ^ 4 + .5) / 10 ^ 4
820  INPUT "ENTER TITLE   ";AA$
830 J =  PEEK (F + I):K =  INT (J / 16): REM  RETAIN UPPER 4 BITS ONLY
840 L = K -  INT (K / 4) * 4
850  IF L = 0 THEN B = 5
860  IF L = 1 THEN B = 1
870  IF L = 2 THEN B = 0.5
880  IF L = 3 THEN B = 0.1
890 C = 0: IF K > 3 THEN C =  - B
900  IF K < 4 THEN OS = 0
910  RETURN
920  CALL ADRS: REM  INITIALIZE HRCG
930  HGR : POKE 49234,0
940  HCOLOR= 3
950  REM SWITCH TO ALL HIGH RESOLUTION GRAPHICS
960  HPLOT 23,27 TO 23,155 TO 279,155
970 A$ = "1"
980  REM DRAW AXES
990  PRINT A$
1000  REM CALL CHARACTER SET
1010  VTAB 2: HTAB 6: PRINT "INTEGRATION TIME ";H2;" SECS"
1020  HTAB 6: PRINT AA$
1030 Y = 20
1040  VTAB Y: HTAB 4: PRINT "!"
1050  VTAB Y: HTAB 13: PRINT "&"
1060  VTAB Y: HTAB 22: PRINT "'"
1070  VTAB Y: HTAB 31: PRINT "("
1080  VTAB Y: HTAB 40: PRINT ")"
1090  REM PRINT THE INDEX MARKS FOR THE ABSCISSA
1100  FOR A = 0 TO 2:: VTAB (20 - A * 8): PRINT (C + (B - C) * A / 2): NEXT A
1110  VTAB 6: PRINT "V": VTAB 7: PRINT "O": VTAB 8: PRINT "L": VTAB 9: PRINT "T"
: VTAB 10: PRINT "S"
1120  REM LABEL THE ORDINATE
1130  FOR BB = 0 TO 8: HTAB 4: VTAB (4 + BB * 2): PRINT "%": NEXT BB
1140  REM PRINT THE INDEX MARKS FOR THE ORDINATE
1150 CC = 21
1160  VTAB CC: HTAB 4: PRINT "0"
1170  VTAB CC: HTAB 12: PRINT "32"
1180  VTAB CC: HTAB 21: PRINT "64"
1190  VTAB CC: HTAB 30: PRINT "96"
```

```
1200  VTAB CC: HTAB 38: PRINT "128"
1210  VTAB 22: HTAB 17: PRINT "DIODE #"
1220  VTAB 23: HTAB 17: PRINT "ARRAY #";I
1230  REM LABEL THE ABSCISSA
1240  HPLOT 23,3
1250 M = 128:N = 256:O = 768:S = 32
1260 T = 23:U = 155
1270 P = G + M * I:Q = P + O
1280  FOR KK = 1 TO M:R = M - KK:X = T + 2 * KK
1290 H1 =  PEEK (P + R) + N *  PEEK (Q + R)
1300 J1 = 4096:K1 = 65536: IF H1 > J1 THEN H1 =  - (K1 - H1)
1310 H1 = H1 + OS
1320 HH =  INT (H1 / S)
1330 Y = U - HH
1340 X = T + KK * 2
1350  ONERR  GOTO 1500
1360  HPLOT  TO X,Y: NEXT KK
1370  REM PLOT OUT THE DATA AS A GRAPHS
1380  RETURN
1390  IF Z > 2 THEN 1430
1400  GOSUB 790
1410  GOSUB 920
1420  GOTO 400
1430  IF Z > 3 THEN 1460
1440  GOTO 90
1450  PRINT
1460  PRINT "PRESS RESET FOLLOWED BY RUNDRS"
1470  PRINT
1480  PRINT "THE DATA IS NOT OVER WRITTEN IMMEDIATELY BY RUN DRS AND CAN BE PROC
ESSED THROUGH OTHER OUTPUTS"
1490  STOP
1500  GOTO 440
```

SEL6 allows data to be saved on a disk in drive #2. It saves both the data file and the gain and replicate data information as a second file on a single instruction. It suggests a simple coding system to help subsequent identification of the type of data being saved. Spaces and other delimiting characters should not be used in file names as they tend to get forgotten and the files have to be identified absolutely to read from them. Data for all 6 arrays are saved at once. A means file takes up a total of 10 sectors on the disk and a raw data file requires 13 sectors.

```
10  HIMEM: 29439
20  REM PROGRAM **SEL6**
30  HOME
40  VTAB 2: PRINT "THIS OPTION ALLOWS DATA TO BE SAVED ON A"
50  PRINT "A DISKETTE IN DRIVE #2": PRINT
60  PRINT "DATA IS SAVED IN A BINARY FILE........": PRINT
70  PRINT "..........SUPPLEMENTARY INFORMATION ON": PRINT
80  PRINT "INTEGRATION TIMES, REPLICATIONS AND": PRINT
90  PRINT "A/DC SETTINGS IS ALSO SAVED AND": PRINT
100  PRINT "RELOADED WITH THE SAME COMMAND": PRINT : PRINT
110  PRINT "THE FILE NAME MUST CONTAIN INFORMATION": PRINT
120  PRINT "THAT DESCRIBES THE TYPE OF DATA SAVED":
130  VTAB 24: PRINT "(PRESS SPACE BAR TO CONTINUE)"
140  CALL  - 756
150  HOME
160  PRINT "A FILE NAME MAY CONTAIN UP TO 30": PRINT
170  PRINT "CHARACTERS STARTING WITH A LETTER": PRINT
180  PRINT "THE FOLLOWING SIMPLE CODE IS SUGGESTED": PRINT
190  HTAB 4: PRINT "S......SIGNAL DATA": PRINT
200  HTAB 4: PRINT "B......BACKGROUND DATA": PRINT
210  HTAB 4: PRINT "D......DIFFERENCE(SUBTRACTED VALUES)": PRINT
220  HTAB 4: PRINT "R......RAW DATA": PRINT
230  HTAB 4: PRINT "M......MEAN VALUES": PRINT
240  HTAB 4: PRINT "C......CALIBRATION FILE": PRINT
250  PRINT "START A FILE NAME WITH CODE LETTERS": PRINT
260  PRINT "FOLOWED BY A LABEL": PRINT
270  INPUT "ENTER FILE NAME";F$
280 G$ = F$ + "Z"
290  REM FILE G$ HOLDS THE DATA COLLECTION PARAMETERS
300  HOME
310  VTAB 2: PRINT "ORIGIN OF DATA TO BE SAVED:-": PRINT
320  HTAB 4: PRINT "1. IN THE INPUT BUFFER": PRINT
330  HTAB 4: PRINT "2. BACKGROUND RAW DATA FILE": PRINT
340  HTAB 4: PRINT "3. ANALYTE DATA MEANS FILE": PRINT
350  HTAB 4: PRINT "4. BACKGROUND DATA MEANS FILE": PRINT
360  HTAB 4: PRINT "5. THE SET OF DATA THAT HAS JUST BEEN"
370  HTAB 7: PRINT "DISPLAYED ON THIS SCREEN OR ON AN": PRINT
380  HTAB 7: PRINT "OSCILLOSCOPE OR RECORDER": PRINT
390  PRINT
400  INPUT "ENTER1,2,3,4 OR 5";S$
410  HOME
420  ON  VAL (S$) GOTO 450,460,470,480,450
430  REM   B=START OF DATA,C=START OF CODE FILE,L=LENGTH OF DATA FILE
440  REM CODE FILE IS ALWAYS 24 BYTES LONG
450 B = 32768:C = 32513:L = 2304: GOTO 490
460 B = 35072:C = 32550:L = 2304: GOTO 490
470 B = 30976:C = 32574:L = 1536: GOTO 490
480 B = 29440:C = 32598:L = 1536: GOTO 490
490  PRINT  CHR$ (4);"BSAVE";F$;",D2,A";B;",L"L
500  PRINT  CHR$ (4);"BSAVE";G$;",A";C;",L24"
510  PRINT  CHR$ (4);"BLOADTEST,D1"
520  PRINT  CHR$ (4);"RUNDRS"
```

SEL7 displays the data stored in the input buffer on an oscilloscope, array by array. The oscilloscope should be switched to inverse polarity. The program requires that the digital to analog converter located in the start pulse indicator box be powered. The DAC is wired four bits higher on the interface board than the data in the buffer. Consequently MC12.OBJ0 is used to move all the data in the buffer 4 bits higher at the start of the display and MC12B.OBJ0 moves the data 4 bits lower at the end.

Program MC12A.OBJ0 is the display program. It uses a software generated strobe to enable the latches feeding data to the DAC and generates a trigger for the oscilloscope by means of two successive software operations. The strobe and trigger come from the Apple through the game I/O connector.

```
10  HIMEM: 29439
20  REM PROGRAM **SEL7**
30  HOME
40  PRINT "THIS OPTION DISPLAYS THE DATA STORED IN": PRINT
50  PRINT "THE INPUT BUFFER ON AN OSCILLOSCOPE": PRINT
60  PRINT "THE ARRAYS ARE DISPLAYED SINGLY": PRINT
70  PRINT "*************************************"
80  PRINT  CHR$ (4);"BRUNMC12.OBJ0,D1"
90  REM SHIFT DATA IN THE BUFFER 4 BITS HIGHER
100  PRINT
110  PRINT "THE DISPLAY FOR EACH ARRAY WILL CONTINUE": PRINT
120  PRINT "UNTIL ANY KEY IS DEPRESSED": PRINT
130  INPUT "ENTER ARRAY # (IF >5 IT RETURNS TO MAIN MENU)";I
140  REM  CONNECT DAC LINES TO ALL PB OUTPUTS AND UPPER 4 PA OUTPUTS
150  IF I > 5 THEN 280
160  HOME
170  INVERSE : PRINT "TURN ON THE D/AC POWER SUPPLY BY PUTTING THE SWITCH AT THE
 BACK OF THE GREY BOX IN THE UP POSITION": PRINT
180  PRINT "PUT SELECT SWITCH IN SCOPE POSITION": PRINT
190  NORMAL
200  PRINT
210 A = 32768:B = 768:C = 128:D = A + I * C:E = D + B:F = 256
220 DH =  INT (D / F):DL = D - DH * F:EH =  INT (E / F):EL = E - EH * F
230  POKE 32622,DL: POKE 32623,DH: POKE 32624,EL: POKE 32625,EH
240  REM THE START ADDRESSES FOR THE DATA TO BE DISPLAYED
250  PRINT  CHR$ (4);"BRUNMC12A.OBJ0"
260  REM RUN THE DISPLAY PROGRAM
270  GOTO 100
280  PRINT  CHR$ (4);"BRUNMC12B.OBJ0"
290  REM SHIFT DATA IN THE BUFFER 4 BITS LOWER
300  PRINT  CHR$ (4);"RUNDRS"
```

```
SOURCE FILE: MC12
----- NEXT OBJECT FILE NAME IS MC12.OBJ0
9200:                       ORG  $9200
9200:               *PROGRAM TO SHIFT 12 BITS OF DATA 4 BITS HIGHER
9200:A2 00                  LDX  #$00
9202:A0 04            BR1   LDY  #$04       ;LOAD THE NUMBER OF SHIFTS TO BE MADE
9204:1E 00 80         BR2   ASL  $8000,X    ;SHIFT LOW BYTE ONE BIT
9207:               *TO THE LEFT AND PUT THE MSB INTO THE CARRY FLAG
9207:3E 00 83               ROL  $8300,X    ;SHIFT THE HIGH BYTE ONE BIT
920A:               *TO THE LEFT ANDPICK UP THE CARRY INTO THE LSB
920A:1E 00 81               ASL  $8100,X
920D:3E 00 84               ROL  $8400,X
9210:1E 00 82               ASL  $8200,X
9213:3E 00 85               ROL  $8500,X
9216:88                     DEY             ;DECREMENT THE SHIFT COUNTER
9217:D0 EB                  BNE  BR2        ;SHIFT AGAIN IF NECESSARY
9219:CA                     DEX             ;CHANGE TO THREE NEW DATA POINTS
921A:D0 E6                  BNE  BR1
921C:60                     RTS             ;BACK TO BASIC
```

```
SOURCE FILE: MC12A
----- NEXT OBJECT FILE NAME IS MC12A.OBJ0
9200:                   ORG  $9200
9200:          *OUTPUT TO OSCILLOSCOPE
9200:          *ENTER STARTING ADDRESSES FOR DATA FOR INDIVIDUAL ARRAYS
C400:          PORT     EQU  $C400      ;LABEL THE INPUT OUTPUT SLOT
9200:AD 6E 7F           LDA  $7F6E      ;LOAD THE LOW BYTE OF THE
9203:          *ADDRESS OF THE LOW BYTE BASE ADDRESS FOR THE ARRAY DATA
9203:8D 29 92           STA  ADD1+1     ;WRITE IT FORWARD IN THE PROGRAM
9206:AD 6F 7F           LDA  $7F6F      ;LOAD THE HIGH BYTE OF THE
9209:          *ADDRESS OF THE LOW BYTE BASE ADDRESS FOR THE ARRAY DATA
9209:8D 2A 92           STA  ADD1+2     ;WRITE IT FORWARD IN THE PROGRAM
920C:AD 70 7F           LDA  $7F70      ;LOAD THE LOW BYTE OF THE
920F:          *ADDRESS OF THE HIGH BYTE BASE ADDRESS FOR THE ARRAY DATA
920F:8D 2F 92           STA  ADD2+1     ;WRITE IT FORWARD IN THE PROGRAM
9212:AD 71 7F           LDA  $7F71      ;LOAD THE HIGH BYTE OF THE
9215:          *ADDRESS OF THE HIGH BYTE BASE ADDRESS FOR THE ARRAY DATA
9215:8D 30 92           STA  ADD2+2     ;WRITE IT FORWARD IN THE PROGRAM
9218:          *TRIGGER THE SCOPE WITH A SOFTWARE GENERATED STROBE
9218:AD 5B C0  BR2      LDA  $C05B
921B:AD 5A C0           LDA  $C05A
921E:          *SET DDRAS FOR ALL OUTPUTS
921E:A9 FF              LDA  #$FF
9220:8D 12 C4           STA  PORT+$12
9223:8D 13 C4           STA  PORT+$13
9226:A2 7F              LDX  #$7F       ;SET UP FOR 128 DIODES
9228:          *READ AND THEN OUTPUT LOW AND HIGH BYTES
9228:BD AA AA  ADD1     LDA  $AAAA,X
922B:8D 11 C4           STA  PORT+$11
922E:BD AA AA  ADD2     LDA  $AAAA,X
9231:8D 10 C4           STA  PORT+$10
9234:AD 40 C0           LDA  $C040      ;NEGATIVE STROBE TO ENABLE THE LATCHES
9237:CA                 DEX
9238:10 EE              BPL  ADD1
923A:          *LOOK FOR KEYBOARD INPUT TO END CYCLING
923A:AD 00 C0           LDA  $C000
923D:30 03              BMI  BR3
923F:4C 18 92           JMP  BR2        ;TRIGGER AGAIN
9242:AD 10 C0  BR3      LDA  $C010
9245:          *BACK TO BASIC PROGRAM
9245:60                 RTS

SOURCE FILE: MC12B
----- NEXT OBJECT FILE NAME IS MC12B.OBJ0
9200:                   ORG  $9200
9200:          *PROGRAM TO SHIFT 12 BIT VALUES 4 BITS LOWER (REVERSE OF MC12
)
9200:A2 00              LDX  #$00
9202:A0 04     BR1      LDY  #$04       ;LOAD THE NUMBER OF SHIFTS TO BE MADE
9204:5E 00 83  BR2      LSR  $8300,X    ;SHIFT HIGH BYTE ONE BIT
9207:          *TO THE RIGHT AND PUT THE LSB INTO THE CARRY FLAG
9207:7E 00 80           ROR  $8000,X    ;SHIFT LOW BYTE ONE BIT
920A:          *TO THE RIGHT AND PICK UP THE CARRY INTO THE MSB
920A:5E 00 84           LSR  $8400,X
920D:7E 00 81           ROR  $8100,X
9210:5E 00 85           LSR  $8500,X
9213:7E 00 82           ROR  $8200,X
9216:88                 DEY             ;DECREMENT THE SHIFT COUNTER
9217:D0 EB              BNE  BR2        ;SHIFT AGAIN IF NECESSARY
9219:CA                 DEX             ;CHANGE TO THREE NEW DATA POINTS
921A:D0 E6              BNE  BR1
921C:60                 RTS             ;BACK TO BASIC
```

SEL8 is similar to SEL7 except that the output rate of the data values is slowed down to suit the response speed of a chart recorder. The data output rate can be altered by the user. If the buffer values are the result of a subtraction, there will be some values below zero because of noise. These values appear in the data as having high values in the most significant nibble of the high byte. This makes a mess of the output.

MC21.OBJ0 allows the addition of an offset value to bring all data values positive first.

MC13.OBJ0 is the display program incorporating nested loops to slow down the output rate.

```
10  HIMEM: 29439
20  REM PROGRAM **SEL8**
30  HOME
40  PRINT "THIS OPTION DISPLAYS THE DATA STORED IN": PRINT
50  PRINT "THE INPUT BUFFER ON A CHART RECORDER": PRINT
60  PRINT "THE ARRAYS ARE DISPLAYED SINGLY": PRINT
70  PRINT "****************************************"
80  PRINT : PRINT "ENTER RECORDER RESPONSE SPEED"
90  PRINT : PRINT "IN POINTS PER MINUTE": PRINT : PRINT "MINIMUM 40": INPUT L
100  IF L < 40 GOTO 90
110  POKE 32627, INT (9710 / L)
120  REM  POKES THE VALUE FOR THE INNER LOOP COUNTER INTO
130  REM SCRATCHPAD MEMORY
140  PRINT "IF BUFFER IS LOADED ENTER 1"
150  PRINT : PRINT "IF DATA IS ON DISKETTE ENTER 2"
160  INPUT A$
170  ON  VAL (A$) GOTO 240,190
180  REM LOAD THE BUFFER FROM A DISK
190  INPUT "ENTER FILE NAME";F$
200 G$ = F$ + "Z"
210  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$8000"
220  PRINT  CHR$ (4);"BLOAD";G$;",A$7F01"
230  PRINT  CHR$ (4);"BLOADTEST,D1"
240  PRINT : PRINT "IF DATA IS THE RESULT OF A "
250  PRINT "SUBTRACTION ENTER 1"
260  PRINT : PRINT "IF NOT THEN ENTER 2"
270  PRINT : INPUT B$
280  ON  VAL (B$) GOTO 330,370
290  PRINT
300  REM IF A SUBTRACTION WAS USED NOISE WILL CAUSE SOME NEGATIVE
310  REM VALUES TO BE IN THE BUFFER AND THIS CAUSES A DISASTER
320  REM TO PREVENT THIS ADD AN OFFSET VALUE TO THE BUFFER DATA
330  PRINT "ENTER OFF SET 1 TO 255  "
340  INPUT H
350  POKE 32628,H
360  PRINT  CHR$ (4);"BRUNMC21.OBJ0"
370  PRINT  CHR$ (4);"BRUNMC12.OBJ0"
380  REM SHIFT DATA IN THE BUFFER 4 BITS HIGHER
390  INPUT "ENTER ARRAY # (IF >5 IT RETURNS TO MAIN MENU)";I
400  IF I > 5 THEN 530
410  HOME
420  INVERSE : PRINT "TURN ON THE D/AC POWER SUPPLY BY PUTTING THE SWITCH AT THE
 BACK OF THE GREY BOX IN THE UP POSITION": PRINT
430  PRINT "PUT SELECT SWITCH IN RECORDER POSITION": PRINT
440  PRINT "PRESS SPACE BAR TO START": NORMAL
450  CALL  - 756
460 A = 32768:B = 768:C = 128:D = A + I * C:E = D + B:F = 256
470 DH =  INT (D / F):DL = D - DH * F:EH =  INT (E / F):EL = E - EH * F
480  POKE 32622,DL: POKE 32623,DH: POKE 32624,EL: POKE 32625,EH
490  PRINT
500  PRINT  CHR$ (4);"BRUNMC13.OBJ0"
510  REM OUTPUT THE DATA TO THE RECORDER
520  GOTO 390
530  PRINT  CHR$ (4);"BRUNMC12B.OBJ0"
540  REM SHIFT DATA IN THE BUFFER 4 BITS LOWER
550  PRINT  CHR$ (4);"RUNDRS"
```

```
SOURCE FILE: MC21
----- NEXT OBJECT FILE NAME IS MC21.OBJ0
9200:            1          ORG  $9200
9200:            2 *PROGRAM TO ADD AN OFFSET VALUE TO THE INPUT BUFFER DATA
9200:            3 *VALUES PRIOR TO PLOTTING ON A CHART RECORDER. BASIC
9200:            4 *PROGRAM HAS PREVIOUSLY POKED THE OFFSET VALUE INTO
9200:            5 *ADDRESS $7F74 (32628)
9200:A2 00       6          LDX  #$00      ;ZERO COUNTER
9202:18          7 BR1      CLC            ;CLEAR CARRY FLAG
9203:BD 00 80    8          LDA  $8000,X   ;LOAD DATA LOW BYTE
9206:6D 74 7F    9          ADC  $7F74     ;ADD THE OFFSET
9209:9D 00 80   10          STA  $8000,X   ;STORE THE SUM
920C:BD 00 83   11          LDA  $8300,X   ;LOAD DATA HIGH BYTE
920F:69 00      12          ADC  #$00      ;ADD THE VALUE OF THE CARRY FLAG
9211:9D 00 83   13          STA  $8300,X   ;STORE AGAIN
9214:18         14          CLC
9215:BD 00 81   15          LDA  $8100,X
9218:6D 74 7F   16          ADC  $7F74
921B:9D 00 81   17          STA  $8100,X
921E:BD 00 84   18          LDA  $8400,X
9221:69 00      19          ADC  #$00
9223:9D 00 84   20          STA  $8400,X
9226:18         21          CLC
9227:BD 00 82   22          LDA  $8200,X
922A:6D 74 7F   23          ADC  $7F74
922D:9D 00 82   24          STA  $8200,X
9230:BD 00 85   25          LDA  $8500,X
9233:69 00      26          ADC  #$00
9235:9D 00 85   27          STA  $8500,X
9238:CA         28          DEX            ;DECREMENT COUNTER
9239:D0 C7      29          BNE  BR1       ;GO ROUND AGAIN IF NOT FINISHED
923B:60         30          RTS            ;RETURN TO BASIC
```

```
SOURCE FILE: MC13
----- NEXT OBJECT FILE NAME IS MC13.OBJ0
9200:            1          ORG  $9200
9200:            2 *OUT PUT TO CHART RECORDER
9200:            3 *ENTER STARTING ADDRESSES FOR DATA FOR INDIVIDUAL ARRAYS
C400:            4 PORT     EQU  $C400      ;LABEL THE INPUT/OUTPUT SLOT
9200:AD 6E 7F    5          LDA  $7F6E      ;LOAD THE LOW BYTE OF THE
9203:            6 *ADDRESS OF THE LOW BYTE BASE ADDRESS FOR THE ARRAY DATA
9203:8D 23 92    7          STA  ADD1+1     ;WRITE IT FORWARD IN THE PROGRAM
9206:AD 6F 7F    8          LDA  $7F6F      ;LOAD THE HIGH BYTE OF THE
9209:            9 *ADDRESS OF THE LOW BYTE BASE ADDRESS FOR THE ARRAY DATA
9209:8D 24 92   10          STA  ADD1+2     ;WRITE IT AHEAD IN THE PROGRAM
920C:AD 70 7F   11          LDA  $7F70      ;LOAD THE LOW BYTE OF THE
920F:           12 *ADDRESS OF THE HIGH BYTE BASE ADDRESS FOR THE ARRAY DATA
920F:8D 29 92   13          STA  ADD2+1     ;WRITE IT FORWARD IN THE PROGRAM
9212:AD 71 7F   14          LDA  $7F71      ,LOAD THE HIGH BYTE OF THE
9215:           15 *ADDRESS OF THE HIGH BYTE BASE ADRESS FOR THE ARRAY DATA
9215:8D 2A 92   16          STA  ADD2+2     ;WRITE IT FORWARD IN THE PROGRAM
9218:A9 FF      17          LDA  #$FF
921A:8D 12 C4   18          STA  PORT+$12
921D:8D 13 C4   19          STA  PORT+$13
9220:A2 7F      20          LDX  #$7F       ;SET UP FOR 128 DIODES
9222:           21 *READ AND THEN OUTPUT LOW AND HIGH BYTES
9222:BD AA AA   22 ADD1     LDA  $AAAA,X
9225:8D 11 C4   23          STA  PORT+$11
9228:BD AA AA   24 ADD2     LDA  $AAAA,X
922B:8D 10 C4   25          STA  PORT+$10
922E:AD 40 C0   26          LDA  $C040      ;NEGATIVE STROBE TO ENABLE THE LATCHES
9231:           27 *ENTER DELAY LOOP TO SUIT THE SLOW RESPONSE OF THE RECORDER"
9231:           28 *LOAD THE NUMBER OF CYCLES IN THE INNER LOOP
9231:A9 00      29          LDA  #$00
9233:8D 72 7F   30          STA  $7F72
9236:A0 00      31          LDY  #$00       ;ZERO THE INNER LOOP CYCLE COUNTER
9238:18         32 BR4      CLC             ;ENTER THE OUTER LOOP
9239:A9 00      33          LDA  #$00
923B:18         34 BR5      CLC             ;ENTER THE INNER LOOP
923C:69 01      35          ADC  #$01
923E:48         36          PHA             ;WASTE SOME TIME
923F:68         37          PLA
9240:48         38          PHA
9241:68         39          PLA
9242:CD 72 7F   40          CMP  $7F72
9245:D0 F4      41          BNE  BR5        ;END OF INNER LOOP CYCLE
9247:C8         42          INY             ;COUNT THE INNER LOOP CYCLE
9248:CC 73 7F   43          CPY  $7F73      ;COMPARE TO THE REQUIRED NUMBER
924B:D0 EB      44          BNE  BR4        ;COMPLETE DELAY CYCLE
924D:CA         45          DEX
924E:10 D2      46          BPL  ADD1       ;FETCH ANOTHER DATA POINT
9250:60         47          RTS             ;BACK TO BASIC
```

SEL9 lists the data values array by array and allows them to be printed out. All values are given in voltages.

SEL10 pair averages the input buffer turning 128 data points into 127 two point averages. The program is useful to reduce the odd-even pattern before displaying the data values.

MC20.OBJ0 carries out the averaging in machine code. The effect is shown in Figure 59.

SEL11 calculates the peak height against a selected background calculated from off-peak diodes. The background selection used depends upon the quality of the observed background. It calculates standard deviations of the background and the signal to noise ratio based on the background variability. It also calculates the peak height in terms of volts per second of integration time. The program will hang if a single off-peak diode is used as a background value.

SEL12 calculates concentrations from peak heights using data obtained from calibration standards. Concentrations are calculated by linear interpolation (or extrapolation) from two calibration standards, one of which may be zero.

```
10  HIMEM: 29439
20  REM PROGRAM **SEL9**
30  REM THIS OPTION LISTS THE DIODE DATA VALUES FOR A SINGLE ARRAY.
40  REM IT ALSO ALLOWS A PRINTOUT OF THE VALUES
50  HOME
60  PRINT "THIS OPTION DISPLAYS VALUES AS VOLTAGES"
70  PRINT
80  PRINT
90  PRINT "DATA CAN BE:-
100  PRINT "1. SINGLE RUN IN THE INPUT BUFFER"
110  PRINT
120  PRINT
130  PRINT "2. SINGLE RUN IN THE BACKGROUND DATA"
140  HTAB 4: PRINT "FILE"
150  PRINT
160  PRINT "3. SUBTRACTED MEAN VALUES STORED"
170  HTAB 4: PRINT "IN THE INPUT BUFFER"
180  PRINT
190  PRINT "4. ANALYTE SIGNAL MEANS"
200  PRINT
210  PRINT "5. BACKGROUND MEAN VALUES"
220  PRINT
230  PRINT "6. FROM A DISKETTE IN DRIVE #2"
240  PRINT
250  INPUT "ENTER 1,2,3,4,5 OR 6  ";E$
260  ON  VAL (E$) GOTO 280,290,300,310,320,330
270  REM F=BASE ADDRESS FOR THE GAIN CODES AND G= BASE ADDRESS FOR THE DATA
280 F = 32525:G = 32768: GOTO 400
290 F = 32562:G = 35072: GOTO 400
300 F = 32525:G = 32768: GOTO 400
310 F = 32586:G = 30976: GOTO 400
320 F = 32610:G = 29440: GOTO 400
330  INPUT "ENTER FILE NAME  ";F$
340  REM LOAD FROM DISKETTE TO INPUT BUFFER
350 G$ = F$ + "Z"
360  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$8000"
370  PRINT  CHR$ (4);"BLOAD";G$;",A$7F01"
380  PRINT  CHR$ (4);"BLOADTEST,D1"
390 F = 32525:G = 32768
400 H = 16:P = 4096:D = 256:E = 768:M = 1:R = 128
410  INPUT "ENTER ARRAY #  ";I
420 J =  PEEK (F + I):K =  INT (J / H): REM RETAIN UPPER 4 BITS ONLY
430 L = K -  INT (K / 4) * 4
440  IF L = 0 THEN B = 5
450  IF L = 1 THEN B = 1
460  IF L = 2 THEN B = 0.5
470  IF L = 3 THEN B = 0.1
480 C = 0: IF K > 3 THEN C =  - B
490 Q = (B - C) / P: REM VALUE OF LSB
500  PRINT "CHOOSE"
510  HTAB 4: PRINT "1. SELECT A GROUP OF DIODES (MAX 23)": PRINT
520  HTAB 4: PRINT "2. DISPLAY ALL DIODES.USE CONTROL S": PRINT
530  HTAB 7: PRINT "TO STOP DISPLAY TO READ": PRINT
540  INPUT "SELECT 1 OR 2  ";A$
550  ON  VAL (A$) GOTO 560,610
560  PRINT : INPUT "ENTER # OF FIRST DIODE  ";W
570  PRINT : INPUT "ENTER # OF LAST DIODE   ";V
580  IF V - W > 22 THEN  PRINT ;"TOO MANY FOR THE SCREEN": GOTO 560
590  GOSUB 630
600  GOTO 740
```

```
610 W = 1:V = 128: GOSUB 630
620  GOTO 740
630  PRINT "ARRAY # ";I
640  FOR J = W TO V
650 U = R - J:N = G + I * R:O = N + E
660 S =  PEEK (N + U) + D *  PEEK (O + U)
670  IF S > P - M THEN S = S - D * D
680  REM CORRECT FOR VALUES BELOW ZERO
690 T = S * Q + C:T =  INT (T * 10 ^ 5 + .5) /  INT (10 ^ 5)
700  REM  CALCULATE THE VOLTAGE AND ROUND OFF TO 5 DECIMAL PLACES
710  PRINT "# ";J;"  ";T;"VOLTS"
720  NEXT J
730  RETURN
740  CALL  - 756: HOME
750  PRINT "SELECT:-": PRINT
760  HTAB 4: PRINT "1. RETURN TO MAIN MENU": PRINT
770  HTAB 4: PRINT "2. ANOTHER ARRAY ": PRINT
780  HTAB 4: PRINT "3. ANOTHER FILE ": PRINT
790  HTAB 4: PRINT "4. MAKE A PRINTED COPY": PRINT
800  INPUT "ENTER 1,2,3 OR 4  ";B$
810  ON  VAL (B$) GOTO 820,410,90,830
820  PRINT  CHR$ (4);"RUNDRS"
830  PRINT  CHR$ (4);"PR#1": GOSUB 630
840  PRINT  CHR$ (4);"PR#0": GOTO 740
```

```
10  HIMEM: 29439: HOME
20  REM PROGRAM **SEL10**
30  PRINT "THIS OPTION PAIR AVERAGES THE INPUT"
40  PRINT "BUFFER. DIODE N AND DIODE N+1 ARE"
50  PRINT "AVERAGED AND STORED AS DIODE N."
60  PRINT "THIS MEANS THAT ONE SIGNAL IS LOST"
70  PRINT "PER ARRAY. IGNORE THE 128TH VALUE"
80  INVERSE : PRINT : PRINT "THE CONTENTS OF THE INPUT BUFFER "
90  PRINT "WILL BE LOST .IF NECESSARY ABORT "
100  PRINT "THIS OPTION AND SAVE IT ON DISKETTE "
110  PRINT : PRINT
120  NORMAL : PRINT "IS BUFFER ALREADY LOADED?"
130  PRINT "TYPE 1 IF YES, 2 IF NO"
140  INPUT Z
150  IF Z <  > 2 THEN  GOTO 210
160  INPUT "LOAD FILE FROM DRIVE 2, ENTER FILE NAME ";F$
170 G$ = F$ + "Z"
180  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$8000"
190  PRINT  CHR$ (4);"BLOAD";G$;",            A$7F01"
200  PRINT  CHR$ (4);"BLOADTEST,D1"
210  PRINT : PRINT "PRESS SPACE BAR TO CONTINUE"
220  CALL  - 756
230  PRINT
240  PRINT  CHR$ (4);"BRUNMC20.OBJ0"
250  FOR I = 0 TO 5:B = I * 128: POKE 32895 + B,0: POKE 33663 + B,0: NEXT
260  PRINT  CHR$ (4);"RUNDRS"
```

```
SOURCE FILE: MC20
----- NEXT OBJECT FILE NAME IS MC20.OBJ0
9200:              1         ORG  $9200
9200:              2 *PROGRAM TO PAIR AVERAGE THE INPUT BUFFER
9200:A2 00         3         LDX  #$00       ;SET INDEX TO ZERO
9202:              4 *ADD TWO BYTE TOGETHER
9202:18            5 BR1     CLC             ;CLEAR THE CARRY FLAG
9203:BD 00 80      6         LDA  $8000,X    ;LOAD LOW BYTE OF A DATA POINT
9206:7D 01 80      7         ADC  $8001,X    ;ADD THE LOW BYTE OF THE NEXT
9209:9D 00 80      8         STA  $8000,X    ;STORE AS THE LOW BYTE OF THE ORIGINAL
920C:              9 *DATA POINT
920C:BD 00 83     10         LDA$8300,X ;LOAD THE HIGH BYTE OF A DATA POINT
920F:7D 01 83     11         ADC  $8301,X    ;ADD THE HIGH BYTE OF THE NEXT
9212:9D 00 83     12         STA  $8300,X    ;STORE AS THE HIGH BYTE OF ORIGINAL
9215:             13 *DATA POINT
9215:             14 *AVERAGE THEM
9215:5E 00 83     15         LSR  $8300,X    ;DIVIDE BY TWO
9218:7E 00 80     16         ROR  $8000,X
921B:18           17         CLC
921C:BD 00 81     18         LDA  $8100,X
921F:7D 01 81     19         ADC  $8101,X
9222:9D 00 81     20         STA  $8100,X
9225:BD 00 84     21         LDA  $8400,X
9228:7D 01 84     22         ADC  $8401,X
922B:9D 00 84     23         STA  $8400,X
922E:5E 00 84     24         LSR  $8400,X
9231:7E 00 81     25         ROR  $8100,X
9234:18           26         CLC
9235:BD 00 82     27         LDA  $8200,X
9238:7D 01 82     28         ADC  $8201,X
923B:9D 00 82     29         STA  $8200,X
923E:BD 00 85     30         LDA  $8500,X
9241:7D 01 85     31         ADC  $8501,X
9244:9D 00 85     32         STA  $8500,X
9247:5E 00 85     33         LSR  $8500,X
924A:7E 00 82     34         ROR  $8200,X
924D:E8           35         INX             ;INCREMENT THE INDEX
924E:D0 B2        36         BNE  BR1        ;DO SOME MORE AVERAGING
9250:60           37         RTS             ;BACK TO BASIC
```

```
10  HIMEM: 29439: HOME
20  REM PROGRAM **SEL11**
30  REM CALCULATE PEAK HEIGHT AGAINST SELECTED BACKGROUND VALUES
40  DIM V1(12),B1(12)
50  GOTO 190
60  REM  DECODE THE INTEGRATION TIME
70 H =  PEEK (F + I + I) + D *  PEEK (F + I + I + C):K = H * P
80  REM  DECODE THE GAIN CODE
90 J =  INT (( PEEK (F + L + I)) / E)
100 N = J -  INT (J / M) * M
110  IF N = 0 THEN O = 5
120  IF N = 1 THEN O = 1
130  IF N = 2 THEN O = 0.5
140  IF N = 3 THEN O = 0.1
150 Q = 0: IF J > 3 THEN Q =  - O
160 R = (O - Q) / S
170  REM THE VALUE OF THE LSB
180  RETURN
190 B = 768:C = 1:D = 256:E = 16:L = 12:M = 4:P = 3.1289E - 3:S = D * E:T = 128:
T1 = 4095
200  PRINT "THIS OPTION OBTAINS A DATA VALUE": PRINT
210  PRINT "FROM A FILE BY SUBTRACTING BACKGROUND": PRINT
220  PRINT "VALUES FROM THE SAME FILE": PRINT
230  PRINT : PRINT "THE DATA  FILE CAN BE": PRINT
240  PRINT "1. IN THE INPUT BUFFER AS A SINGLE RUN"
250  PRINT "   OR AS MEANS"
260  PRINT : PRINT "2. IN THE ANALYTE MEANS FILE": PRINT
270  PRINT "3. ON A DISKETTE IN DRIVE # 2"
280  INPUT "ENTER 1,2 OR 3  ";B$
290  REM LOCATE THE DATA FILE
300  ON  VAL (B$) GOTO 390,310,330
310 F = 32574:G = 30976: GOTO 400
320  REM  LOAD FILE FROM DISKETTE
330  INPUT "ENTER FILE NAME  ";F$
340 G$ = F$ + "Z"
350  PRINT  CHR$ (4);"BLOAD";F$;",D2,A$8000"
360  PRINT  CHR$ (4);"BLOAD";G$;",A$7F01"
370  PRINT  CHR$ (4);"BLOADTEST,D1"
380 N1 = 8
390 F = 32513:G = 32768
400  PRINT
410  PRINT : PRINT : PRINT "----------------------------------------"
420  PRINT "THE METHOD DEPENDS ON THE BACKGROUND"
430  PRINT : PRINT "1. WHERE THE BACKGROUND LEVEL IS FLAT": PRINT
440  PRINT "2. WHERE THE BACKGROUND IS FLAT "
450  HTAB 5: PRINT "BUT ODD EVEN PATTERN IS SERIOUS"
460  PRINT "3. WHERE A SPECIAL BACKGROUND "
470  HTAB 5: PRINT "IS TO BE USED"
480  PRINT
490  INPUT "ENTER CORRESPONDING NUMBER  ";A$
500  REM SELECT THE TYPE OF BACKGROUND AVAILABLE
510  INPUT "ENTER ARRAY # 0 TO 5  ";I
520 B2 = G + T * I:B3 = B2 + B
530  PRINT : IF I > 5 GOTO 510
540  INPUT "ENTER DIODE #OF PEAK 1 TO 128  ";A
550  GOSUB 60
560 U = T - A:V =  PEEK (G + T * I + U) + D *  PEEK (G + B + T * I + U)
570  IF V > T1 THEN V = V - D * D
580  ON  VAL (A$) GOTO 590,650,710
590 B1(0) = A - 11:B1(1) = A - 10:B1(2) = A - 9:B1(3) = A - 8
600 B1(4) = A + 8:B1(5) = A + 9:B1(6) = A + 10:B1(7) = A + 11
```

```
610 N1 = 8
620  GOSUB 950
630  GOSUB 830
640  GOTO 1040
650 B1(0) = A - 14:B1(1) = A - 12:B1(2) = A - 10:B1(3) = A - 8
660 B1(4) = A + 8:B1(5) = A + 10:B1(6) = A + 12:B1(7) = A + 14
670 N1 = 8
680  GOSUB 950
690  GOSUB 830
700  GOTO 1040
710  PRINT "ENTER DIODE #'S OF BACKGROUND"
720  PRINT "UP TO 12 NUMBERS EACH ONE FOLLOWED BY A RETURN"
730  PRINT "AFTER LAST DIODE NUMBER ENTER 'END'"
740  INVERSE : PRINT "PROGRAM NEEDS AT LEAST 2 VALUES": NORMAL
750  REM IF ONLY ONE VALUE USED THE PROGRAM WILL HANG
760 K1 = 0
770  INPUT AB$: IF AB$ = "END" THEN  GOTO 790
780 B1(K1) =  VAL (AB$):K1 = K1 + 1: GOTO 770
790 N1 = K1
800  GOSUB 950
810  GOSUB 830
820  GOTO 1040
830  REM  SUBROUTINE TO CALCULATE MEAN AND SD
840  REM  VALUES IN V1(12)
850  REM  NO. OF VALUES IN N1
860  REM  RETURNS MEAN IN M1 AND SD IN S1
870 I1 = 0:J1 = 0
880  FOR L1 = 0 TO N1 - 1
890 I1 = I1 + V1(L1)
900 J1 = J1 + (V1(L1)) ^ 2
910  NEXT L1
920 M1 = I1 / N1
930 S1 =  SQR ((J1 - (I1 ^ 2) / N1) / (N1 - 1))
940  RETURN
950  REM  SUBROUTINE TO PUT BACKGROUND DIODE VALUES INTO V1(12)
960  REM  NUMBER OF VALUES IS IN N1
970  REM  POSITIONS OF BACKGROUND RELATIVE TO PEAK IS IN B1(12)
980  REM  RETURNS BACKGROUND DIODE VALUES IN V(12)
990  FOR K1 = 0 TO N1 - 1
1000 U1 = T - B1(K1):V1(K1) =  PEEK (B2 + U1) + D *  PEEK (B3 + U1)
1010  IF V1(K1) > T1 THEN V1(K1) = V1(K1) - D * D
1020  NEXT K1
1030  RETURN
1040  INPUT "ENTER TITLE";C$
1050  PRINT  CHR$ (4);"PR#1"
1060  PRINT C$
1070  PRINT F$
1080  PRINT "  ARRAY #  ";I
1090  PRINT "  DIODE #  ";A
1100  PRINT "  BACKGROUND METHOD  ";A$
1110  REM VALUES ROUNDED OUT TO 5 DECIMAL PLACES
1120  PRINT "  PEAK HT.  "; INT ((V - M1) * R * 10 ^ 5 + .5) / (10 ^ 5)
1130  PRINT "INTEGRATION TIME =  ";K;" SECONDS"
1140  PRINT "BACKGROUND MEAN "; INT ((M1 * R + Q) * 10 ^ 5 + .5) / (10 ^ 5)
1150  PRINT "  STANDARD DEVIATION OF BACKGROUND "; INT ((S1 * R) * 10 ^ 7 + .5)
/ (10 ^ 7)
1160  PRINT "  S/NR   "; INT (((V - M1) / S1) * 10 ^ 5 + .5) / (10 ^ 5)
1170  PRINT "  "; INT ((R * (V - M1) / K) * 10 ^ 7 + .5) / (10 ^ 7);" VOLTS PER
SEC OF INTEGRATION"
1180  PRINT : PRINT
1190  PRINT  CHR$ (4);"PR#0"
1200  GOTO 20
```

```
10  HIMEM: 29439: HOME
20  REM PROGRAM **SEL12**
30  REM CALCULATE CONCENTRATIONS FROM PEAK HEIGHTS AND
40  REM CALIBRATION VALUES
50  PRINT "THIS OPTION CALCULATES SOLUTION "
60  PRINT : PRINT "CONCENTRATIONS FROM VOLTAGE": PRINT
70  PRINT "OUTPUTS BY LINEAR INTERPOLATION"
80 N = 1: PRINT
90  INPUT "ENTER ELEMENT NAME. IF DONE ENTER DONE     ";A$(N)
100  IF A$(N) = "DONE" GOTO 200
110  INPUT "ENTER HIGH STD CONC IN PPM  ";X
120 X(N) = X
130  INPUT "ENTER HIGH READING IN VOLTS  ";R
140 R(N) = R
150  INPUT "ENTER LOW STD CONC IN PPM  ";T$
160  REM IF NO ENTRY IS MADE FOR A LOW STD ZERO IS ASSUMED
170 T(N) =  VAL (T$)
180  INPUT "ENTER LOW READING IN VOLTS  ";Z$
190 Z(N) =  VAL (Z$):N = N + 1: GOTO 90
200 G = N - 1: FOR N = 1 TO G: PRINT N;"  ";A$(N): PRINT : NEXT N
210  INPUT "ENTER SOLUTION NAME              ";B$
220  PRINT  CHR$ (4);"PR#1": PRINT B$;
230  PRINT  CHR$ (4);"PR#0"
240  INPUT "ENTER ELEMENT #  ";N
250  INPUT "ENTER READING IN VOLTS  ";Q(N)
260 Q = Q(N):R = R(N):T = T(N):X = X(N):Z = Z(N)
270 M(N) = ((X - T) * Q + R * T - Z * X) / (R - Z)
280  REM CALCULATE THE CONCENTRATION
290  PRINT  CHR$ (4);"PR#1"
300  PRINT A$(N);"  CONC = ";M(N);"  PPM"
310  PRINT  CHR$ (4);"PR#0"
320  GOTO 240
```

ARRAYSET is a BASIC program that produces a list of the useful lines for the elements to be considered in first, second and third order. The program lists them in spectral order over the range governed by the physical size and shape of the direct reader. The original source of the data is the tables published by Winge, Peterson and Fassel [43]. These have been entered on a disk as a series of text files by use of the program ELEMENTINPUT. The text files are labelled by the atomic symbol of the element and the number of lines (of all 3 orders) listed. Lines not listed in the Winge tables are not included.

The ARRAYSET program combines the text files into a dimensional array within a single text file and then order sorts them using QUICKSORTHIGH, a version of a fast machine code sorting program developed by Bongers [50].

The output for each line gives the order in sequence, the spectral position, the element and the symbol for ion or atomic line, the wavelength of the parent first order line, the detection limit from the Winge table in ppb and a number of stars corresponding to the order.

The program has several options, allowing a printout of the listing,and if required, information on the restrictions on the placement of the spectral windows due to the dimensions of the array and its carriage.

```
10  REM PROGRAM **ARRAYSET** TO HELP POSITION THE ARRAYS
20  INVERSE : PRINT "WARNING ": NORMAL
30  PRINT "THERE IS A CHARACTER IN THIS PROGRAM": PRINT
40  REM THE DOS DOESN'T HANDLE THE AMPERSAND WELL
50  PRINT "THAT THE D.O.S. CAN'T HANDLE"
60  PRINT : PRINT "SO PRESS CONTROL C AND RETURN"
70  PRINT : PRINT "AND TYPE:-"
80  PRINT : HTAB 10: PRINT "640&SQRG$"
90  PRINT : HTAB 10: PRINT "RUN"
100  PRINT : PRINT "IF YOU HAVE JUST LOADED IT"
110  PRINT : PRINT
120  CLEAR
130 D$ =  CHR$ (4)
140  PRINT D$;"BRUNQUICKSORTHIGH"
150  REM QUICKSORT IS NOT REPRODUCED FOR COPYRIGHT REASONS.SEE REF 50
160  DIM C$(70)
170  REM ALLOWS UP TO 70 SETS OF ELEMENTAL LINES
180 I = 0
190  FOR N = 1 TO 70
200  INPUT "ENTER ELEMENT FILE NAME (ENTER DONE IF  FINISHED )";C$(N)
210  REM THE FILE NAME MUST BE TAKEN FROM THE DISK CATALOG
220  IF C$(N) = "DONE" GOTO 260
230 I = I + 1
240  NEXT N
250  REM ENTER NUMBER OF ELEMENTS
260 J = I
270 A = 0
280  FOR P = 1 TO J
290 A$ = C$(P)
300  REM SELECT ELEMENTAL FILES IN ORDER
310  FOR R = 3 TO 1 STEP  - 1
320 B$ =  RIGHT$ (A$,R)
330  IF  VAL (B$) > 0 GOTO 360
340  REM FINDS THE NUMBER OF LINES IN EACH FILE
350  NEXT R
360 A = A +  VAL (B$)
370  REM SUM ALL THE NUMBERS OF LINES
380  NEXT P
390  DIM G$(A)
400  REM SET THE DIMENSION TO HOLD ALL THE LINES IN THE FILE
410 I = 1
420  FOR S = 1 TO J
430  REM DISPLAY THE ELEMENTAL FILE NAME
440 A$ = C$(S)
450  PRINT A$
460  FOR T = 3 TO 1 STEP  - 1
470 B$ =  RIGHT$ (A$,T)
480  IF  VAL (B$) > 0 GOTO 500
490  NEXT T
500 B =  VAL (B$)
510  REM FIND THE NUMBER OF LINES IN THE FILE
520 C = I:D = C + B - 1
530  PRINT  CHR$ (4);"OPEN";A$
540  REM OPEN THE MAIN TEXT FILE
550  PRINT D$;"READ";A$
560  FOR I = C TO D
570  INPUT G$(I)
580  REM PUT THE FILE LINES INTO THE MAIN TEXT FILE
590  NEXT I
600  PRINT D$;"CLOSE";A$
```

```
610  REM CLOSE THE MAIN TEXT FILE
620  NEXT S
630  REM  CONTINUE
640  &  SQR G$
650  REM RUN THE SORT PROGRAM
660  GOSUB 680
670  GOTO 720
680  FOR I = 1 TO A: PRINT I;"  ";G$(I): NEXT I
690  REM LIST ALL LINES IN SPECTRAL ORDER
700  CALL  - 756
710  RETURN
720  HOME
730  PRINT "CHOOSE:-": PRINT
740  HTAB 4: PRINT "1. PRINT IT OUT": PRINT : HTAB 4: PRINT "2. POSITION ARRAYS"
: PRINT
750  HTAB 4: PRINT "3. MAKE ANOTHER SELECTION": PRINT : HTAB 4: PRINT "4. GOODBY
E": PRINT
760  INPUT "ENTER 1,2,3 OR 4  ";E
770  ON E GOTO 780,850,820,840
780  PRINT  CHR$ (4);"PR#1": GOSUB 680
790  REM PRINT OUT HARD COPY
800  PRINT  CHR$ (13); CHR$ (4);"PR#0"
810  GOTO 720
820  GOTO 120
830  REM CHOOSE ANOTHER SET OF ELEMENTS
840  END
850  HOME
860  PRINT "AN ARRAY COVERS A SPECTRAL WINDOW OF 17"
870  REM PROGRAM EXCLUDES UNAVAILABLE POSITIONS
880  PRINT : PRINT "ANGSTROM UNITS."
890  PRINT : PRINT "ARRAYS CAN ONLY BE SPACED AT SPECTRAL": PRINT
900  PRINT "INTERVALS OF 250 ANGSTROM UNITS.": PRINT
910  PRINT "ACTUAL PHYSICAL POSITION ON THE CIRCLE": PRINT : PRINT "WILL BE GIVE
N ELSEWHERE": PRINT
920  PRINT "ARRAYS ARE NUMBERED FROM 0 TO 5"
930  INVERSE : PRINT "BE READY TO PRESS CTRL-S": NORMAL
940 F2 = 0
950  FOR G = 0 TO 5
960  PRINT "ENTER SPECTRAL POSITION ARRAY #  ";G: INPUT F
970  PRINT  CHR$ (4);"PR#1": PRINT F: IF F < F2 THEN  PRINT "IMPOSSIBLE TO LOCAT
E": PRINT  CHR$ (4);"PR#0": GOTO 960
980 F1 = F + 17:F2 = F + 250
990  PRINT  CHR$ (4);"PR#0"
1000  FOR I = 1 TO A
1010  IF  VAL (G$(I)) < F GOTO 1060
1020  IF  VAL (G$(I)) > F2 GOTO 1050
1030  IF  VAL (G$(I)) > F1 GOTO 1060
1040  PRINT  CHR$ (4);"PR#1": PRINT "WINDOW  ";I;"  ";G$(I): PRINT  CHR$ (4);"PR
#0": NEXT I
1050  PRINT I;"  ";G$(I)
1060  NEXT I
1070  NEXT G
1080  PRINT  CHR$ (4);"PR#0"
1090  GOTO 730
```

LINELOC calculates the position for the array carriage on the direct reader focal plane corresponding to a spectral value.

ELEMENTINPUT is used to enter the information from the Winge table and creates the text files with up to 3 spectral orders for use with ARRAYSET.

Due to the space occupied by the text files, the programs ARRAYSET, LINELOC and ELEMENTINPUT, and the text file library are stored on a disk other than that carrying the direct reader operating system.

The program QUICKSORTHIGH is not reproduced for reasons of copyright. See reference [50].

```
10  REM PROGRAM **LINELOC** TO CONVERT SPECTRAL POSITION TO
20  REM FOCAL PLANE POSITION
30  HOME : PRINT "SPECTRAL LINE LOCATION "
40  PRINT "POSITIONS FOR THE RHS OF MOUNT"
50 D = 149.1776:CV = 4707.24
60 C = 58.8
70  INPUT "ENTER WAVELENGTH REQUIRED IN ANGSTROM UNITS";AV
80  INPUT "ENTER SPECTRAL ORDER  ";T
90 AV = AV * T
100 S = (CV - AV) * 118 / 10 ^ 6
110 F =  ATN (S /  SQR ( - S * S + 1))
120 G = D * S + C
130  PRINT  CHR$ (4);"PR#1"
140  PRINT AV;"ANGSTROMS  = ";G;" CMS ON SCALE"
150  PRINT  CHR$ (4);"PR#0"
160  GOTO 70
170  REM THIS GIVES A REASONABLE FIT
```

```
10  REM PROGRAM **ELEMENTINPUT** TO ENTER SPECTRAL LINE INFORMATION
20  CLEAR
30  INPUT "ENTER ATOMIC SYMBOL  ";A$
40  INPUT "ENTER NUMBER OF LINES";Q
50 N = Q * 3: DIM G$(N)
60 I = 1
70  FOR P = 1 TO Q: PRINT "ENTER LINE TYPE,WAVELENGTH IN AU,LIMITS IN PPB.
80  PRINT "(TO END ENTER...END,0,0)
90  INPUT B$,C$,D$
100  IF B$ = "END" GOTO 230
110  FOR E = 1 TO 3:F$ =  STR$ (E *  VAL (C$))
120  IF  VAL (F$) > 7620 GOTO 210
130  ON E GOTO 140,150,160
140 E$ = "*": GOTO 170
150 E$ = "**": GOTO 170
160 E$ = "***"
170 G$(I) = F$ + " " + A$ + " " + B$ + " " + C$ + " " + D$ + " " + E$
180 I = I + 1
190 M = I - 1
200  NEXT E
210  PRINT
220  NEXT P
230  GOSUB 250
240  GOTO 360
250  REM STORE LINE INFO IN A TEXT FILE
260 D$ =  CHR$ (4)
270  PRINT D$;"OPEN";A$
280  PRINT D$;"WRITE";A$
290  FOR I = 1 TO M
300  PRINT G$(I)
310  NEXT I
320  PRINT D$;"CLOSE";A$
330 M$ =  STR$ (M):I$ = A$ + M$
340  PRINT D$;"RENAME";A$;",";I$
350  RETURN
360  GOTO 20
```

APPENDIX 7

APPENDIX 7

POWER SUPPLIES FOR THE SIX ARRAY SYSTEM

The Apple computer came with a built in power supply that supplied:-

+5 V, 2.5 A
-5 V, .25 A
+11.8 V, 1.5 A
-12 V, .250 A

The power for the six RC1024S array control boards and their auxiliary circuitry required:-

+5 V, 3.8 A
+15 V, .45 A
-15 V, 1.05 A

These were supplied by a LAMBDA LOT-W5152A power supply.

The 6 sets of Peltier heat pumps together required 6 V, 12 A. This was supplied by two LAMBDA power supplies, an LCS CC 01 and an LCS C 01. One supplied power to 4 sets, the other to 2.

The integration timer circuit board, the digital to analog converter and the integration time indicator system were powered off the +5 V, +15 V and -15 V supply from a HEATH DIGITAL POWER MODULE EU 801-11.